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(54) INK JET RECORDING PAPER, AND INK JET RECORDING METHOD

(57)Abstract:

PROBLEM TO BE SOLVED: To ensure a high water resistance and a high moisture resistance with a small consumption amount of a cationic mordant by making a pH value of a recording surface side film surface of an ink absorbing layer to be a specified value.

SOLUTION: At least one layer of an ink absorbing layer containing a hydrophilic binder and a cationic mordant having a mordant force for an anionic dye, is provided on a supporting body, and the film surface pH on the recording surface side of the ink absorbing layer is made 3 or higher and 5 or lower. When the film surface pH is less than 3, the water resistance and the moisture resistance are improved, but when an ink jet recording is performed, a dye coagulates on the moment when a recording liquid comes into contact with the surface of a recording paper, or the dye is deposited on the surface by time passing after a recording, and a favorable maximum concentration cannot be obtained, and a color tone defect may be generated. Also, when the film surface pH exceeds 5, the water resistance and the moisture resistance become insufficient, and especially the reduction of the moisture resistance is large. Therefore, the best water resistance and moisture resistance can be obtained by using a minimum necessity amount of the cationic mordant, and a defect due to the usage of a large amount of the cationic mordant can be prevented from arising.

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CLAIMS

[Claim(s)]

[Claim 1] The ink jet record form characterized by having at least one layer of ink absorption layers containing the cation mordant which has mordacity to a hydrophilic binder and an anionic color on a base material, and making the film surface pH by the side of the recording surface of an ink absorption layer into 3 or more and 5 or less.

[Claim 2] The ink jet record form according to claim 1 characterized by for the mean particle diameter of a primary particle containing [an ink absorption layer] a non-subtlety particle 30nm or less, and forming the opening.

[Claim 3] The ink jet record form according to claim 2 characterized by non-subtlety particles being at least one sort of non-subtlety particles chosen from the silica compounded by the gaseous-phase method, colloidal silica, an alumina, and hydrated alumina.

[Claim 4] The ink jet record form according to claim 1 to 3 with which a cation mordant is characterized by average molecular weight being 50,000 or less water-soluble mordant.

[Claim 5] The ink jet record form according to claim 1 to 4 with which the amount of a cation mordant is characterized by being 0.01-0.3 in a weight ratio to a non-subtlety particle.

[Claim 6] The ink jet record form according to claim 1 to 5 with which a hydrophilic binder is characterized by being polyvinyl alcohol.

[Claim 7] The ink jet record form according to claim 6 characterized by an ink absorption layer containing a way acid or way sand.

[Claim 8] The ink jet record form according to claim 1 to 7 with which a base material is characterized by being a non-absorptivity base material.

[Claim 9] The ink jet record approach that pH is characterized by what is recorded with the recording ink it is [recording ink] 3 or more and 8 or less at an ink jet record form according to claim 1 to 8.

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TECHNICAL FIELD

[Industrial Application] This invention relates to the ink jet record form which improved the water resisting property and moisture resistance of an image after record in more detail about the ink jet record form which records an image using the ink containing water soluble dye.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the ink jet record form which improved the water resisting property and moisture resistance of an image after record in more detail about the ink jet record form which records an image using the ink containing water soluble dye.

[0002]

[Description of the Prior Art] although ink jet record makes the minute drop of ink fly by various working principles, and is made to adhere to record sheets, such as paper, and an image, an alphabetic character, etc. are recorded, a high speed, the low noise, and multiple-colorizing are comparatively easy — etc. — it has the advantage. About the blinding of a nozzle and the maintenance which had become a problem from the former by this method, from both sides of ink and equipment, amelioration progresses and it has spread quickly in various fields, such as various printers, facsimile, and a computer terminal, in current.

[0003] The detail is indicated by the trend (the volume for Koichi Nakamura, March 31, Heisei 7, the Japan science-information incorporated company issue) of for example, an ink jet record technique.

[0004] As a record form used by this ink jet recording method, also when a printing dot laps [that a color tone is brightly skillful and absorption of ink] early, the diffusion to the longitudinal direction of ink flowing out or not spreading and a printing dot is not large [the concentration of a printing dot is high, and] beyond the need, and generally it is required that the circumference should be smooth and should not fade etc.

[0005] As an ink jet record form, various record forms are used from the former. For example, the ink jet record form which painted the ink absorption layer as a record layer on the base material which consists of a regular paper, a hydrophilic binder and various kinds of coated paper which painted the layer which consists of an inorganic pigment (art paper, coat paper, cast coated paper, etc.), various kinds of papers that covered both sides with plastic resin, transparency, or various kinds of opaque plastic film is used further.

[0006] The above-mentioned ink absorption layer is roughly divided into the ink absorption layer of the opening mold which prepared the opening into the ink absorption layer of the swelling mold constituted by the subject in the hydrophilic binder, and the record layer.

[0007] The ink absorption layer of a swelling mold holds ink in a swelling operation of a hydrophilic binder. As a hydrophilic binder, for example Gelatin, polyvinyl alcohol, Polyethylene oxide, a polyvinyl pyrrolidone, a pullulan, a carboxymethyl cellulose, Hydroxyethyl cellulose, a dextran, a dextrin, polyacrylic acid, and its salt, An agar, a kappa carrageenan, lambda-carrageenan, iota-carrageenan, xanthene gum, A polyalkylene oxide system copolymerization polymer given in locust bean gum, an alginic acid, gum arabic, JP,7-195826,A, and a 7-9757 official report, A homopolymer, a copolymer, etc. of the vinyl monomer which has a water-soluble polyvinyl butyral, or a carboxyl group and a sulfonic group given in JP,62-245260,A are independent, or are used combining two or more sorts.

[0008] The ink absorption layer of an opening mold holds ink to the opening formed in the layer, and the opening is usually formed by making various kinds of inorganic solid-state particles and organic solid-state particles contain in a coat.

[0009] If a non-subtlety particle is used and carried out for the above-mentioned purpose, white inorganic pigments, such as precipitated calcium carbonate, whiting, a magnesium carbonate, a kaolin, clay, talc, a calcium sulfate, a barium sulfate, a titanium dioxide, a zinc oxide, zinc hydroxide, zinc sulfide, zinc carbonate, a hydrotalcite, aluminum silicate, the diatom earth, a calcium silicate, a magnesium silicate, synthetic amorphous silica, colloidal silica, an alumina, a colloidal alumina, pseudo-boehmite, an aluminum hydroxide, a lithopone, a zeolite, and a magnesium hydroxide, etc. are mentioned, for example

[0010] Even if it distributes homogeneity in a binder with a primary particle, these non-subtlety particles may form secondary floc, and homogeneity may be made to distribute them in a binder.

[0011] As an organic particle, particles, such as polystyrene, polyacrylic ester, polymethacrylic acid ester, polyacrylamides, polyethylene, polypropylene, a polyvinyl chloride, polyvinylidene chlorides or these copolymers, a urea-resin, and melamine resin, are mentioned, for example.

[0012] In the ink jet recording method, although the color picture of high saturation is obtained when a water-soluble color is used for recording ink, a water resisting property and moisture resistance are inferior. On the other hand — although it excels a water resisting property and in respect of moisture resistance when a pigment is used for recording ink — the spectral extinction property of color material — broadcloth ** — the coloring matter image of high saturation is hard to be obtained.

[0013] In order to improve the water resisting property and moisture resistance at the time of using the recording ink which used the water-soluble color which is inferior in a water resisting property or moisture resistance, the various approaches to which coloring matter is made to fix from the former are proposed.

[0014] An effective means to improve a water resisting property and moisture resistance in these proposals is an approach using the uniform water solution and particle latex of a cationic polymer which have the nitrogen atom of the 3rd class or the 4th class.

[0015] As the former and ink jet recording method or an ink jet record form, To JP,57-36692,A, for example, on stencil paper or a polyethylene terephthalate film base material The ink jet record form which painted the coating liquid containing gelatin and a basic mordant, and was used as the ink absorbing layer The water-color-ink record form which infiltrated polyethyleneimine into paper in JP,53-49113,A The record material which has the electrolyte polymer which has a cation or an anion radical in JP,58-24492,A In JP,63-224988,A, the 1st class thru/or tertiary amine, or quarternary ammonium salt is contained. The charge of a recorded material which has the ink absorbing layer which set pH to 2-8 to JP,63-307979,A The ink jet record sheet which prepared the layer containing the polymer which has the hydrophilic polymer mordant which has the 3rd class or the 4th class nitrogen atom, and a hydrophilic radical In JP,59-198186,A and a 59-198188 official report The charge of a recorded material which made the organic base of polyethyleneimine contain in the coating layer in a base material or on a base material The method of the ink jet recording method using the ink which contains a specific color in JP,60-46288,A, and the record ingredient containing polyamine etc. In JP,61-61887,A, a 61-72581 official report, a 61-252189 official report, and a 62-174184 official report The ink jet record form containing the poly allylamine to JP,61-172786,A the polymer which has an intermolecular hydrogen bridge, and the polymer (a polyethylene glycol —) which does not have a hydrogen bond nature machine among molecules (gelatin, polyethylene RENIMIN, etc.) The ink jet record ingredient which has a layer containing a polyvinyl pyrrolidone etc. The ink jet record form which applies or infiltrated the cationic polymer and the cationic surface active agent on the base material in JP,63-162275,A The record sheet which has the color fixing layer which uses a quarternary-ammonium-salt polymerization object and cation conversion polyvinyl alcohol as a principal component on a plastics base material, and the color transparency and ink absorption layer which were prepared on it is indicated by JP,6-143798,A.

[0016] Furthermore, JP,59-20696,A, a 59-33176 official report, A 59-33177 official report, a 59-96987 official report, a 59-155088 official report, A 60-11389 official report, a 60-49990 official report, a 60-83882 official report, A 60-109894 official report, a 61-277484 official report, a 61-293886 official report, A 62-19483 official report, a 62-198493 official report, a 63-49478 official report, A 63-115780 official report, a 63-203896 official report, a 63-274583 official report, A 63-280681 official report, a 63-260477 official report, JP,1-9776,A, The nitrogen atom of the 3rd class or the 4th class of specification [a 1-24784 official report, a 1-40371 official report, a 3-133686 official report, a 6-234268 official report, and a 7-125411 official report] Adding the polymer or compound which it has all over an ink absorbing layer is indicated.

[0017] Although the technique which fixes the color indicated by this advanced technology can accept appropriate effectiveness from the point of immobilization of a color, it is not necessarily enough.

[0018] Although what is necessary is just to increase the amount of the mordant used in order to raise a water resisting property and moisture resistance using a cationic mordant, it is easy to produce the various faults accompanying increase in quantity of a cation mordant in this case.

[0019] For example, a cation mordant degrades the lightfastness of the color after record, or a lifting and a cone inclination are during preservation about yellow coloring, and such a fault tends to become remarkable with increase of the addition of a mordant.

[0020] Furthermore, when a water-soluble mordant is used as a cation mordant, there is a fault of making curl increasing, degrading the film formation nature of a coat, or bringing about brittleness with increase of an addition. If the latter problem is large and the addition of a mordant makes it increase especially when an ink absorption layer is the thing of a swelling mold, compatibility with other hydrophilic binders will get worse, and film formation nature and brittleness will be degraded. Moreover, when an ink absorption layer is the thing of an opening mold, in order to have to use an opening layer as a thick film, the addition of a mordant increases and it becomes easy to produce curl.

[0021] Moreover, by becoming easy to produce devitrification and sticking of a coat with increase of an addition, when the latex particle by which the emulsion polymerization was carried out as a cation mordant is used and an ink absorption layer is the thing of a swelling mold, when an ink absorption layer is the thing of an opening mold, an opening will be taken up and void volume will be reduced.

[0022] When the above-mentioned trouble was examined, it became clear that it was solvable by making the pH value of the film surface by the side of the recording surface of an ink absorption layer into a specific value.

[0023]

[Problem(s) to be Solved by the Invention] This invention is made in view of the above-mentioned actual condition, and the 1st purpose of this invention is to offer the ink jet record form which can attain a high water resisting property and high moisture resistance by the amount of few cation mordants used. The 2nd purpose is to offer the ink jet record form which controlled the aforementioned various faults brought about by use of a cation mordant.

[0024]

[Means for Solving the Problem] The above-mentioned purpose of this invention is an ink jet record form characterized by having at least one layer of ink absorption layers containing the cation mordant which has mordacity to (1) hydrophilic-property binder and an anionic color on a base material, and making the film surface pH by the side of the recording surface of an ink absorption layer into 3 or more and 5 or less.

(2) An ink jet record form given in the above (1) characterized by for the mean particle diameter of a primary particle containing [an ink absorption layer] a non-subtlety particle 30nm or less, and forming the opening.

(3) Ink jet record form given in the above (2) characterized by non-subtlety particles being at least one sort of non-subtlety particles chosen from the silica compounded by the gaseous-phase method, colloidal silica, an alumina, and hydrated alumina.

(4) An ink jet record form given in either of above-mentioned (1) – (3) to which a cation mordant is characterized by average molecular weight being 50,000 or less water-soluble mordant.

(5) An ink jet record form given in either of above-mentioned (1) – (4) to which the amount of a cation mordant is characterized by being 0.01–0.3 in a weight ratio to a non-subtlety particle.

(6) An ink jet record form given in either of above-mentioned (1) – (5) to which a hydrophilic binder is characterized by being polyvinyl alcohol.

(7) An ink jet record form given in the above (6) characterized by an ink absorption layer containing a way acid or way sand.

(8) An ink jet record form given in either of above-mentioned (1) – (7) to which a base material is characterized by being a non-absorptivity base material.

(9) The above (1) The ink jet record approach that pH is characterized by what is recorded with the recording ink it is [recording ink] 3 or more and 8 or less at an ink jet record form given in either of – (8).

It is alike and is attained more.

[0025] Although the recorded material which controlled generating of the odor accompanying a mordant by containing the 1st class – tertiary amine, or quarternary ammonium salt, and adjusting pH of an ink absorbing layer within the limits of 2–8 is previously indicated by JP,63-224988,A shown as advanced technology, it is not indicated by by making the film surface pH by the side of the recording surface of an ink absorption layer into a specific pH value that a water resisting property and moisture resistance are acquired. Moreover, the example which made the film surface pH by the side of the recording surface of an ink absorption layer the range of 3–5 is not indicated by this official report, either, but there is also no publication which suggests selecting the range of 3–5 which were specified as a film surface pH in it. And even if pH of an ink absorbing layer is in the range of 2–8, when the film surfaces pH by the side of the recording surface of an ink absorption layer are not 3–5, the effectiveness of this invention is not acquired.

[0026] Therefore, as for this invention, the above-mentioned advanced technology differs in the purpose, and, moreover, configurations also differ.

[0027] Hereafter, this invention is explained to a detail.

[0028] In this invention, paper base materials, such as the base material used for an ink jet record form from the former, for example, a regular paper, art paper, coat paper, and cast coated paper, a plastics base material, the paper base material that covered both sides with polyolefine, and the compound base material which stuck these can be used as a base material.

[0029] When you wish to obtain the high smooth nature and the maximum density after high glossiness and record, it is desirable to use a non-absorptivity base material. The paper base material which covered both sides with the base material or polyolefine which consists of plastic film as a non-absorptivity base material is used preferably, and the paper base material which covered both sides with polyolefine is used as most desirable thing.

[0030] As a base material which consists of plastic film, the base material which consists of plastic film, such as a polyethylene film, a polypropylene film, a polystyrene film, a polyethylene terephthalate film, a polyethylenenaphthalate film, a triacetyl cellulose film, a polyvinyl chloride film, a polyimide film, a polycarbonate film, and cellophane, is used preferably, for example.

[0031] These plastic film can use suitably a transparent thing, a translucent thing, and an opaque thing properly according to an application.

[0032] It is also desirable to use white plastic film for a base material. The film which prepared the layer which has white pigments (titanium oxide, barium sulfate, etc.) in the film [which made plastics contain white pigments, such as a small amount of barium sulfate, titanium oxide, and a zinc oxide, as a white film], rear-face, or ink absorption layer side can be used.

[0033] The stencil paper of the paper base material which covered both sides with polyolefine uses wood pulp as the main raw material, if needed, it adds synthetic fibers, such as synthetic pulps, such as polypropylene, or nylon, and polyester, and paper making is carried out. As wood pulp, although both LBKP, LBSP, NBKP, NBSP LDP and NDP LUKP and NUKP can be used, it is desirable to use more many [for a staple fiber] LBKP, NBSP (s), LBSP(s), and NDP(s) and LDP(s). However, it reaches LBSP or the ratio of LDP has 10 % of the weight or more and 70 desirable % of the weight or less.

[0034] Chemical pulp with few impurities (for example, sulfate pulp, sulfite pulp) is desirable, and pulp's is [the pulp which performed bleaching processing and raised the whiteness degree] useful.

[0035] Hara Kaminaka can add suitably flexible-ized agents, such as moisture hold-back agents, such as paper reinforcing agents, such as white pigments, such as sizing compounds, such as a higher fatty acid and an alkyl ketene dimer, a calcium carbonate, talc, and titanium oxide, starch, polyacrylamide, and polyvinyl alcohol, a fluorescent brightener, and polyethylene glycols, a dispersant, and quarternary ammonium salt, etc.

[0036] The freshness of BARUPU used for paper making has desirable 200-500 cc by convention of CSF, and 30 thru/or 70% have the desirable sum of weight % of the 24-mesh residue and weight % of the 42-mesh residue as which the fiber length after beating is specified to JIS-P -8207. In addition, as for weight % of the four-mesh residue, it is desirable that it is 20 or less % of the weight.

[0037] The basis weight of stencil paper has 60 thru/or desirable 250g, and 90 thru/or its 200g are especially desirable. The thickness of stencil paper has 50 thru/or desirable 250 micrometers.

[0038] After a paper-making phase or paper making, stencil paper can carry out calender processing and can also give the Takahira slippage. A stencil paper consistency has 0.7 thru/or common 1.2 g/m² (JIS-P -8118). Furthermore, stencil paper stiffness has 20 thru/or desirable 200g on the conditions specified to JIS-P -8143.

[0039] A surface sizing compound may be applied to a stencil paper front face, and the sizing compound which can be added to said Hara Kaminaka as a surface sizing compound, and the same sizing compound can be used.

[0040] When measured by the hot water extraction method specified by JIS-P -8113, as for pH of stencil paper, it is desirable that it is 5-9.

[0041] although polyethylene is desirable and the polyethylene (LDPE) of a low consistency and the polyethylene (HDPE) of high density are used especially as polyolefine which covers a stencil paper front face and a rear face — other lines — low density polyethylene (LLDPE), polypropylene, etc. can be used.

[0042] As for the polyethylene layer by the side of an ink absorption layer, what added the titanium oxide of a rutile or an anatase mold, and improved opacity and a whiteness degree in polyethylene is desirable as widely performed by the printing paper for photographs. The content of titanium oxide is 5 - 15 % of the weight preferably three to 20% of the weight in general to polyethylene.

[0043] After preparing an ink absorption layer and a back layer, the amount of the polyethylene used of the front flesh side of stencil paper is chosen so that there may be no curl, damp and when it is saved by highly humidization. Usually, let thickness of the polyethylene layer by the side of 20-50 micrometers and a back layer be the range of 10-40 micrometers for the thickness of the polyethylene layer by the side of an ink absorption layer.

[0044] In this invention, the polyethylene covering paper base material which has the following properties can be used preferably.

A lengthwise direction by the reinforcement specified by :JIS-P -8113 in hauling strength ** 2 thru/or 30kg, a longitudinal direction — 20kg** tear: 1 thru/or on the strength — the convention approach by JIS-P -8116 — a lengthwise direction — 10 — or 300g a longitudinal direction — 20 thru/or 400g** Clerks stiffness: — 20-400cm³ / 100** compressibility: — two or more 103 Kgf/cm²** surface smoothness: — the Beck smoothness specified to JIS-P -8119 500 seconds or more Especially, 1000 second or more ** surface roughness : about the wave filtration waviness curve drawn on with a cut-off value [of 0.8mm] conditions from the cross-section curve measured by the approach specified to JIS-B -0610 as 2.5mm of criteria length — wave filtration max — the time of measuring a wave — 100 point of measurement of the arbitration — max — a point 6 micrometers or more less than five pieces [a wave] The surface glossiness which the ten-point average of roughness height measured at the include angle of 75 degrees by the approach specified to less than 4 micrometer** surface glossiness:JIS-Z -8741 Moreover, 30% or more, When it measures by the approach especially indicated by 90% or more ** surface whiteness degree:JIS-Z -8722 preferably and displays 70% or more according to JIS-Z -8729 preferably, Especially 90% or more and (a*, and b*) L* 85% or more (-2 and 2), When it measures by the approach specified to (4, 2) and (4 -8) (-3, -8) being [it / in the color tone of the range surrounded] ** opacity:JIS-P -8138, 50% or more, 90% or more, it is the purposes, such as enlarging bond strength with a record layer 94% or more especially most preferably at a base material, and it is desirable to perform corona discharge treatment, undercoating processing, etc. to a base material in advance of spreading of a record layer.

[0045] The ink jet record form of this invention has at least one-layer ink absorption layer on a base material. This ink absorption layer may be a swelling mold, or may be an opening mold, and may prepare both layer in the same on [a base material] side further.

[0046] A swelling layer is swollen at the same time it extends a liquid ink drop to a moderate size, when a liquid ink drop reaches the target, and it absorbs a liquid ink drop. The water in the ink absorbed by this swelling layer and other organic solvents evaporate gradually after that, and only the color which is finally a non-volatile component is substantially left behind into a coat.

[0047] The ink absorption layer of a swelling mold needs to show high bloating tendency to a liquid ink drop, and the hydrophilic binder in which liquid ink bloating tendency is shown is used as a main constituent. As a hydrophilic binder used preferably For example, gelatin or a gelatin derivative (phenylcarbamoyl-ized gelatin etc.), A polyvinyl pyrrolidone (about 200,000 or more have desirable average molecular weight), a pullulan, Polyvinyl alcohol or its derivative, a polyethylene glycol (100,000 or more have desirable average molecular weight), A carboxymethyl cellulose, hydroxyethyl cellulose, a dextran, A dextrin, polyacrylic acid and its salt, an agar, a kappa carrageenan, lambda-carrageenan, iota-carrageenan, xanthene gum, locust bean gum, A polyalkylene oxide system copolymerization nature polymer given in an alginic acid, gum arabic, JP,7-195826,A, and a 7-9757 official report, Polymers, such as independent or a copolymer which repeats and has these vinyl monomers of the vinyl monomer which has the carboxyl group and sulfonic group of a publication, can be mentioned to a water-soluble polyvinyl butyral or JP,62-245260,A. These hydrophilic binders may be used independently and may use two or more sorts together.

[0048] Since the ink absorption layer of a swelling mold needs to have the early permeability and the bloating tendency over liquid ink, it is desirable to contain at least one sort as which 200,000 or more polyvinyl pyrrolidones are chosen as for molecular weight, and about 50,000 or more polyethylene oxide and molecular weight are chosen for molecular weight from the copolymer of 100,000 or more polyethylene oxide and polypropylene oxide, hydroxyethyl cellulose, and polyacrylamide to the hydrophilic binder of the ink absorption layer of a swelling mold.

[0049] Considering the viewpoint of stabilization high-speed spreading, it is desirable to use reversibly a part of hydrophilic binder in which sol gel transformation is possible, and it is desirable to use at least one sort of gelatin, a gelatin derivative, and a kappa carrageenan from this point.

[0050] As for the binder used for the ink absorption layer of a swelling mold, what has gelatin or a gelatin derivative at least is desirable. The binder of the combination of the combination of gelatin or a gelatin derivative, the combination of a polyvinyl pyrrolidone and a gelatin derivative, polyvinyl alcohol, and its derivative, the combination of a gelatin derivative, a polyvinyl pyrrolidone, and polyvinyl alcohol, gelatin or gelatin, a polyalkylene glycol, and its derivative is used especially for the desirable ink absorption layer of a swelling mold as a binder.

[0051] As gelatin preferably used in the above, usual alkali treatment gelatin and acid-treatment gelatin are mentioned. The isoelectric point can choose the thing of the range of 9-5 suitably, and can use gelatin.

[0052] The gelatin which made the amino group or imino group of gelatin react with isocyanates, such as acid anhydrides, such as phthalic anhydride, and phenyl isocyanate, and made a part of amino group and imino group [at least] inactivate as derivative gelatin is used preferably.

[0053] When an ink absorption layer is a swelling mold, the range of 4-20 micrometers of desiccation thickness of an ink absorption layer is 6-15 micrometers preferably in general.

[0054] When an ink absorption layer is an opening mold, an opening is formed between solid particulates a hydrophilic property or a hydrophobic binder, inorganic, or organic.

[0055] Various methods can perform formation of an opening. The formation approach of the ink absorption layer of a typical opening mold is explained below.

[1] How to apply the uniform coating liquid containing two or more sorts of polymers which carry out phase separation on a base material, make carry out phase separation of these polymers in a desiccation process, and form an opening.

[2] How to apply the coating liquid containing a solid-state particle and a hydrophilic property, or a hydrophobic binder on a base material, to immerse in the liquid containing water or a suitable organic solvent in a record form after desiccation, make dissolve a solid-state particle, and create an opening.

[3] How to apply the coating liquid containing the compound which has the property which carries out heating foaming on a base material, make these compounds foam in a desiccation process, and form an opening into a coat.

[4] How to apply the coating liquid containing a porosity solid-state particle and a hydrophilic binder on a base material, and form an opening between the inside of a porosity particle, or a porosity particle.

[5] the solid-state particle which has the volume more than equivalence in general to a hydrophilic binder — and — or the approach of applying the coating liquid which mixed the oil droplet particle on a base material, and drying and creating an opening between a hydrophilic binder, and a solid-state particle and an oil droplet particle.

[6] The approach mean particle diameter makes the solid-state particle in the coating liquid which made solid-state particle about 0.1 micrometers or less contain condense at the time of adjustment of coating liquid or coat formation, makes a secondary particle or the three-dimensional structure form, and creates an opening.

[0056] It is required it to be possible to add a cation mordant and to be able to adjust surface pH to 3-5 with any means of the above [the opening formation approach in the record form of this invention], although it is good. Moreover, the approach which is not complicated is desirable, considering the viewpoint which the glossiness on the front face of the recording paper is not much reduced, and creates it by low cost.

[0057] As an approach of making the desirable opening which hits carrying out this invention from the above viewpoint forming, the above [5] or the approach of [6] of desirable especially a desirable approach is the approach of [6].

[0058] In the ink absorption layer of an opening mold, a certain thing of the total amount (void volume) of an opening is [1m of record forms] desirable 20ml or more per two.

[0059] Although ink absorptivity is good when void volume is less than two 20 ml/m, and there are few amounts of ink at the time of printing, if the amount of ink increases, ink will not be absorbed completely, but image quality is reduced or it is easy to produce problems, like drying is late.

[0060] Although especially the upper limit of void volume is not restricted, in order for setting thickness of the ink absorption layer of an opening mold to 50 micrometers or less in general not to worsen the physical characteristic of coats, such as a crack, it is required, and it difficult to make void volume into two or less 40 ml/m, considering this point.

[0061] Setting to this invention, void volume is J.TAPPI Paper pulp test method No.51-87 It is expressed with the amount of liquid transition in absorption time amount 2 seconds (ml/m²) when it measures by the approach indicated by the liquid absorptivity test method (Bristow law) of paper and the paper board. In addition, in order to make distinction of measurement area easy, less than 2% of water soluble dye may be made to contain by the above-mentioned measuring method, although pure water (ion exchange water) is used for measurement.

[0062] In the ink absorption layer of an opening mold, the void volume to solid content capacity is called voidage. in this invention, making voidage into 200% or more especially 150% or more does not have a thick kink in thickness superfluously — since it comes out and an opening can be formed efficiently, it is desirable. Although the upper limit of voidage generally receives constraint from the reinforcement and film formation nature of a coat, it is usually less than 400%.

[0063] When making a solid-state particle contain and making the ink absorption layer of an opening mold form, as a solid-state particle, a well-known solid-state particle inorganic [various kinds of] or organic can be conventionally used in an ink jet record form.

[0064] As an example of the non-subtlety particle used for the above-mentioned purpose, white inorganic pigments, such as precipitated calcium carbonate, whiting, a magnesium carbonate, a kaolin, clay, talc, a calcium sulfate, a barium sulfate, a titanium dioxide, a zinc oxide, zinc hydroxide, zinc sulfide, zinc carbonate, a hydrotalcite, aluminum silicate, the diatom earth, a calcium silicate, a magnesium silicate, synthetic amorphous silica, colloidal silica, an alumina, a colloidal alumina, pseudo-boehmite, an aluminum hydroxide, a lithopone, a zeolite, and a magnesium hydroxide, etc. can be mentioned.

[0065] Homogeneity may distribute in the binder with the primary particle, and a non-subtlety particle forms secondary floc and may be distributed by homogeneity in the binder.

[0066] As an example of an organic particle, particles, such as polystyrene, polyacrylic ester, polymethacrylic acid ester, polyacrylamides, polyethylene, polypropylene, a polyvinyl chloride, polyvinylidene chlorides or these copolymers, a urea-resin, or melamine resin, are mentioned.

[0067] In this invention, a non-subtlety particle is desirable, considering the viewpoint that high voidage is obtained.

[0068] As for the above-mentioned inorganic particle, it is desirable that the particle size of a primary particle uses a thing 30nm or less. Especially the particle size of the primary particle of a desirable non-subtlety particle is 20nm or less.

[0069] When the mean diameter of a primary particle uses the particle exceeding 30nm, floc which the cation mordant of a water-soluble polymer mold and condensation become easy to take place, and formed will also be made big and rough, and glossiness will fall.

[0070] Especially although especially the minimum of the particle size of a primary particle is not limited, 3nm or more is 6nm or more in general from the viewpoint on manufacture of a particle.

[0071] The mean particle diameter of a non-subtlety particle observes the particle which appeared in the cross section and front face of an ink absorption layer of the particle itself or an opening mold with an electron microscope, and is called for as the arithmetic average value (individual number average) in quest of the particle size of the particle of 100 arbitration. The particle size of the particle of each [here] is expressed with the diameter when assuming a circle equal to the projected area.

[0072] As a non-subtlety particle, it is desirable that it makes the ratio of the non-subtlety particle which exceeds 30nm in this case 50 or less % of the weight to all inorganic particles although the mean particle diameter of a primary particle is possible also for the non-subtlety particle and mean particle diameter of 30nm or less using together a non-subtlety particle 30nm or more, and 20 or less % of the weight is more desirable.

[0073] Considering the point of that a clear image is recordable, being able to manufacture by low cost that an image with high concentration is formed, as a solid-state particle, it is desirable to use the solid-state particle chosen from the particle silica, the colloidal silica and the alumina, or hydrated alumina compounded by the gaseous-phase method.

[0074] The alumina or hydrated alumina preferably used in this invention is the porosity alumina whose radius is 3-10nm and whose sum of pore volume is 0.2 - 2 ml/g, or its hydrated compound. Pore volume can be measured with a well-known nitrogen adsorption process.

[0075] An alumina or hydrated alumina may be crystallinity, may be amorphous, and can use the thing of the configuration of arbitration, such as an indeterminate form particle, a spherical particle, and a needlelike particle.

[0076] The particle silica compounded by the gaseous-phase method can burn and obtain a silicon tetrachloride at an elevated temperature with hydrogen and oxygen, and is usually silica powder whose particle diameter of a primary particle is 5-500nm. What has the primary particle diameter of 30nm or less especially is desirable in respect of glossiness.

[0077] The particle silica compounded by current and such gaseous-phase method is marketed, and there is various kinds of Aerosil of Japanese Aerosil in a commercial particle silica.

[0078] The colloidal silica preferably used by this invention carries out double decomposition of the specific silicate with an acid etc., or carries out heating aging of the silica gel which is made to pass an ion-exchange-resin layer and is obtained, and is obtained. Using this colloidal silica for an ink jet record form For example, JP,57-14091,A, a 60-219083 official report, A 60-219084 official report, a 61-20792 official report, a 61-188183 official report, A 63-17807 official report, this JP,4-93284,A, a 5-278324 official report, A 6-92011 official report, a 6-183134 official report, a 6-297830 official report, It is indicated by a 7-81214 official report, the 7-101142 official report, the 7-179029 official report, the 7-137431 official report, the international patent public presentation WO 94/No. 26530 official report, etc.

[0079] Although the particle diameter of colloidal silica is 5-100nm, its thing with a particle diameter of 7-30nm is usually desirable.

[0080] The particle silica and colloidal silica which were compounded by the gaseous-phase method may carry out cation conversion of the front face, for example, may process a front face by mineral salt, such as aluminum, calcium, Mg, and Ba.

[0081] Also in the above-mentioned opening morphogenetic substance, a particle silica is desirable especially in this invention, it is most suitable for performing opening formation of the above [6] especially, and a particle is the silica compounded by the gaseous-phase method.

[0082] A hydrophilic binder is used in order to give the property as a coat to the ink absorption layer of the above-mentioned opening mold.

[0083] Although various kinds of well-known binders used for the ink absorption layer of a swelling mold as these binders can be used conventionally, the binder which swells in the early phase where the liquid ink drop which reached the target permeated, and does not take up an opening substantially is desirable. Especially a desirable hydrophilic binder is polyvinyl alcohol of completeness or partial saponification from this point. In addition, cation denaturation polyvinyl alcohol, anion denaturation polyvinyl alcohol, and Nonion denaturation polyvinyl alcohol are also contained in polyvinyl alcohol here.

[0084] Especially as for desirable polyvinyl alcohol, whenever [saponification] are 80 or more partial saponification polyvinyl alcohol or full saponification polyvinyl alcohol.

[0085] a comparatively high-polymer thing [considering the viewpoint in which the polymerization degree of polyvinyl alcohol improves coat brittleness] — good — average degree of polymerization — 1000-5000 — the thing of 2000-4000 is used especially preferably.

[0086] Cation conversion polyvinyl alcohol is polyvinyl alcohol which has the 1-3rd class amino group which is indicated by JP,61-10483,A, and the 4th class ammonium in the principal chain of polyvinyl alcohol, or a side chain, and it is obtained by saponifying the copolymer of the ethylenic unsaturated monomer and vinyl acetate which have a cationic radical.

[0087] As an ethylenic unsaturated monomer which has a cationic radical For example, TORIMECHIRU-(2-acrylamide -2, 2-dimethyl ethyl) ammoniumchloride, TORIMECHIRU-(3-acrylamide -3, 3-dimethyl propyl) ammoniumchloride, N-vinyl imidazole, N-vinyl-2-methylimidazole, N-(3-dimethylaminopropyl) methacrylamide, Hydroxyl ethyl trimethylammonium chloride, TORIMECHIRU-(methacrylamide propyl) ammoniumchloride, N-(1 and 1-dimethyl-3-dimethylaminopropyl) acrylamide, etc. are mentioned.

[0088] the copolymer of the ethylenic unsaturated monomer and vinyl acetate which have a cationic radical — setting — the ratio of a cation denaturation radical content monomer — vinyl acetate — receiving — 0.1-10-

mol % → it is 0.2–5-mol % preferably.

[0089] Although the thing of polymerization degree 500–4000 is used, as for cation denaturation polyvinyl alcohol, 1000–4000 are usually desirable.

[0090] The copolymer of vinyl alcohol which is indicated by the polyvinyl alcohol and JP,61–237681,A which have an anionic radical which is indicated by JP,1–206088,A as anion denaturation polyvinyl alcohol, for example, and the 63–307979 official report, and the vinyl compound which has a water-soluble radical, and the denaturation polyvinyl alcohol which has a water-soluble radical which is indicated by JP,7–285265,A are mentioned.

[0091] The polyvinyl alcohol derivative which added a polyalkylene oxide radical which is indicated by JP,7–9758,A to a part of vinyl alcohol as Nonion denaturation polyvinyl alcohol, for example, and the block copolymer of the vinyl compound and vinyl alcohol which have the hydrophobic radical indicated by JP,8–25795,A are mentioned.

[0092] Although polyvinyl alcohol is mainly used, other hydrophilic binders can also be made to contain as a binder of the ink absorption layer of an opening mold. As for other hydrophilic binders, it is desirable that it is 20 or less % of the weight in general to polyvinyl alcohol.

[0093] When an ink absorption layer is an ink absorption layer of an opening mold, in the case of the approach [5] of differing by the formation approach of an opening and making said opening forming, the weight ratios to the hydrophilic binder of a solid-state particle are 6–100 in general, and, in the case of the approach [6] of making an opening forming, are 2–10.

[0094] In the ink jet record form of this invention, a cation mordant is contained with a hydrophilic binder in an ink absorption layer.

[0095] Although the polymer mordant which has the class [1st] – 3rd class amino group and a quarternary–ammonium–salt radical can be used as a cation mordant, since there being little discoloration by the passage of time and light–fast degradation and the mordanting ability of a color are high enough, the polymer mordant which has a quarternary–ammonium–salt radical is desirable.

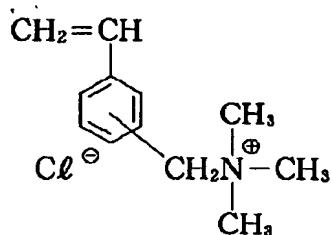
[0096] A desirable polymer mordant is the homopolymer of the monomer which has a quarternary–ammonium–salt radical, a copolymer with other monomers, or a condensation polymerization object.

[0097] The example of the monomer which has the quarternary–ammonium–salt radical preferably used for below is expressed.

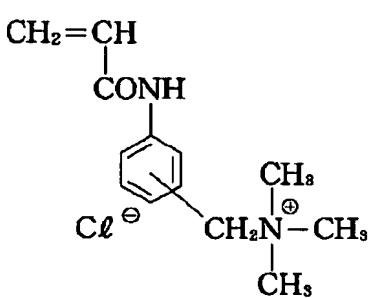
[0098]

[Formula 1]

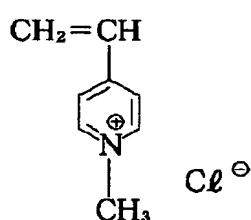
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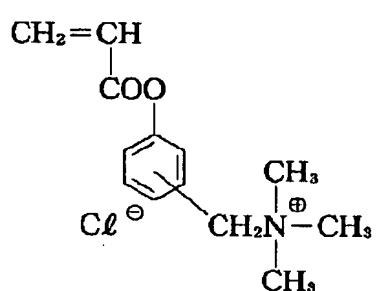
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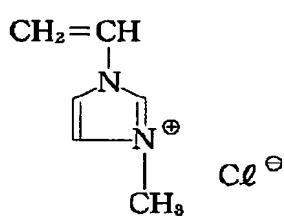
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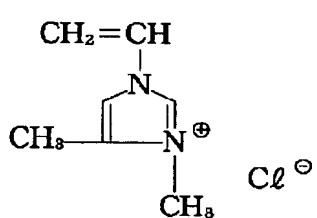
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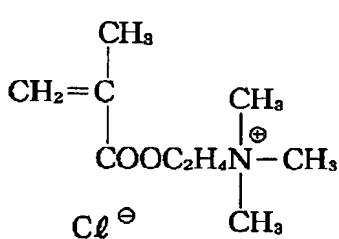
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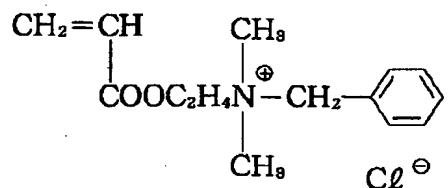
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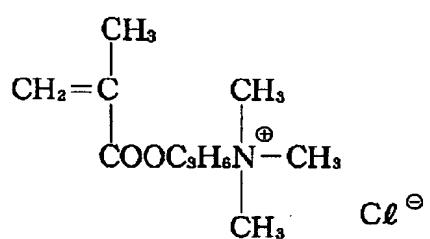
[0099]

[Formula 2]

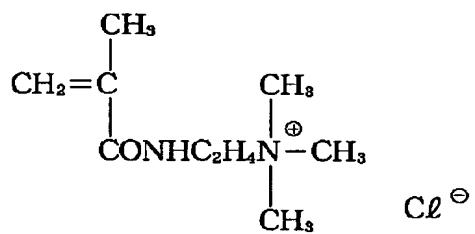
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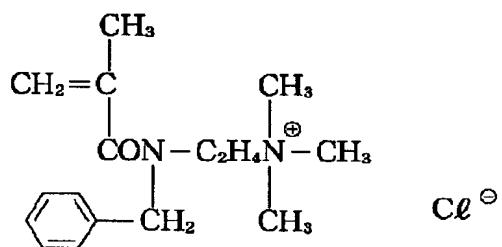
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10



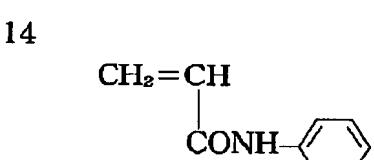
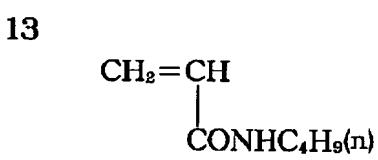
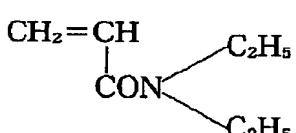
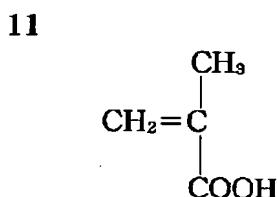
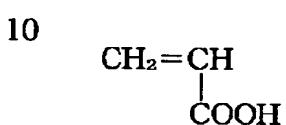
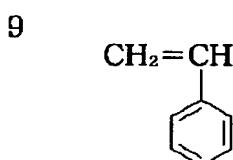
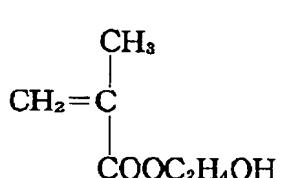
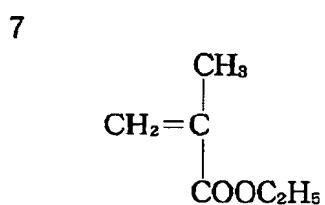
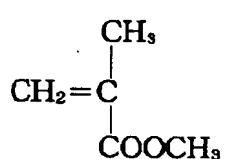
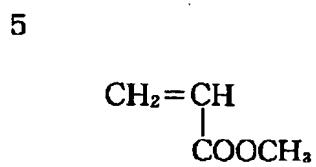
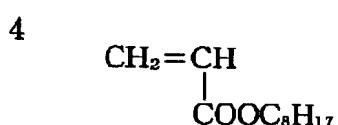
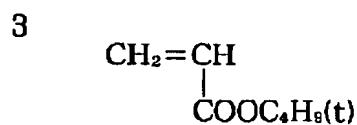
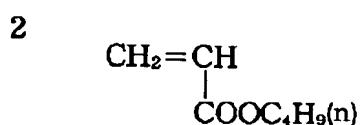
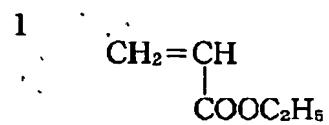
11



上記モノマーと共に重合し得るモノマーの具体例を次に示す。

[0100]

[Formula 3]

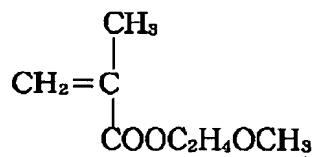


[0101]
[Formula 4]

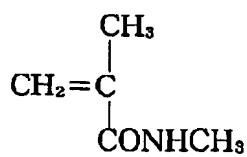
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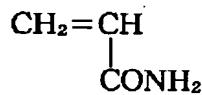
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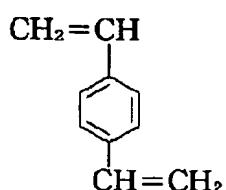
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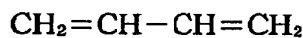
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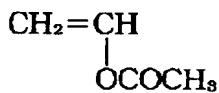
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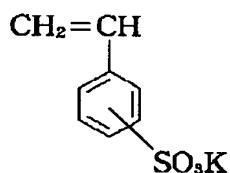
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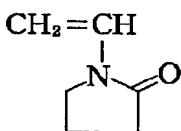
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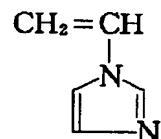
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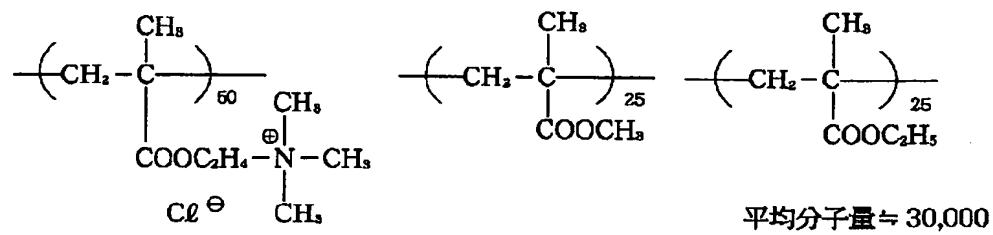


The example of a polymer mordant of having the quarternary-ammonium-salt radical preferably used for below is shown. (A numeric value expresses mol %.)

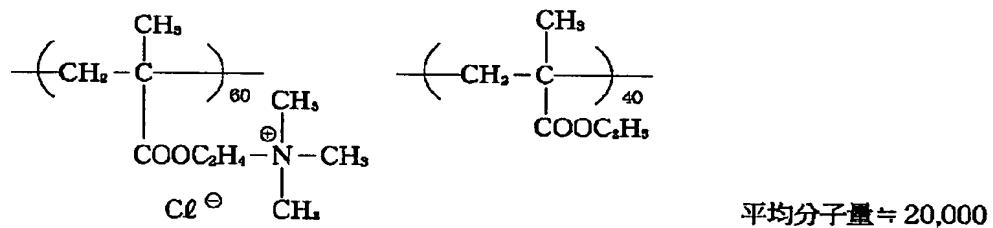
[0102]

[Formula 5]

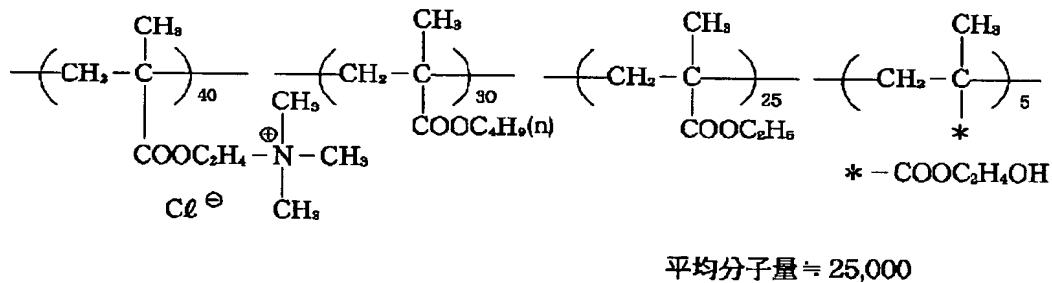
Mor-1



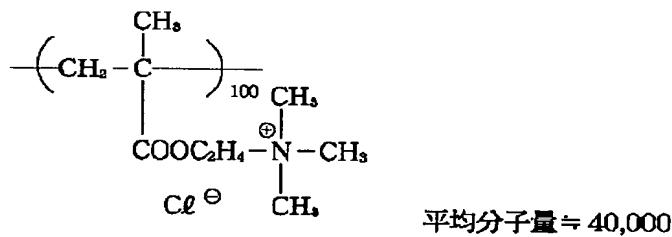
Mor-2



Mor-3



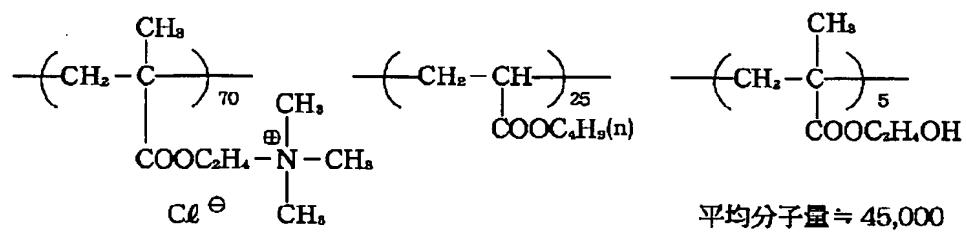
Mor-4



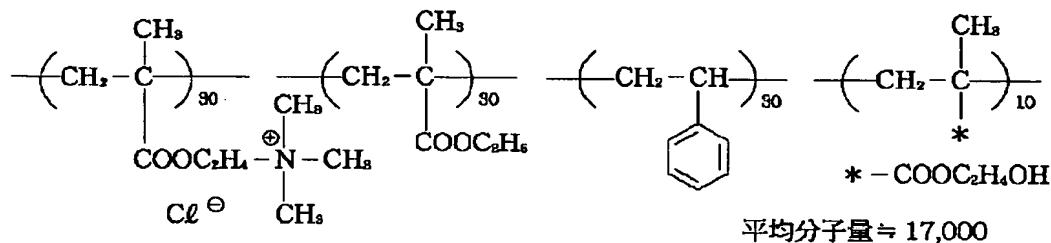
[0103]

[Formula 6]

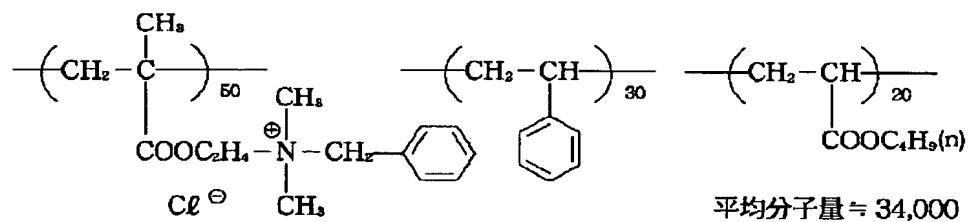
Mor - 5.



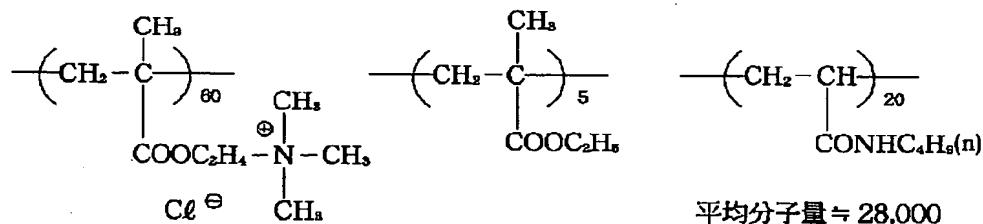
Mor - 6



Mor - 7

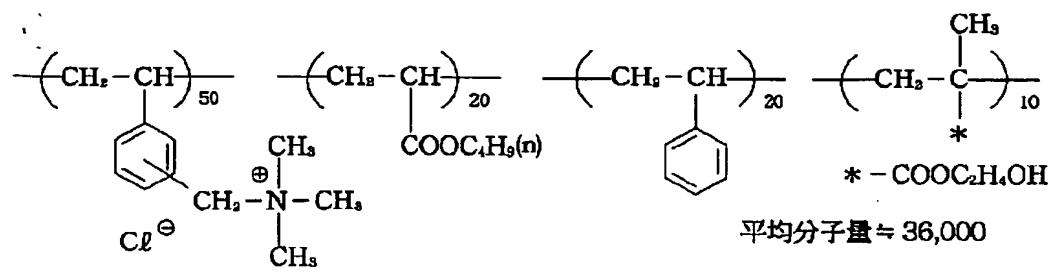


Mor - 8

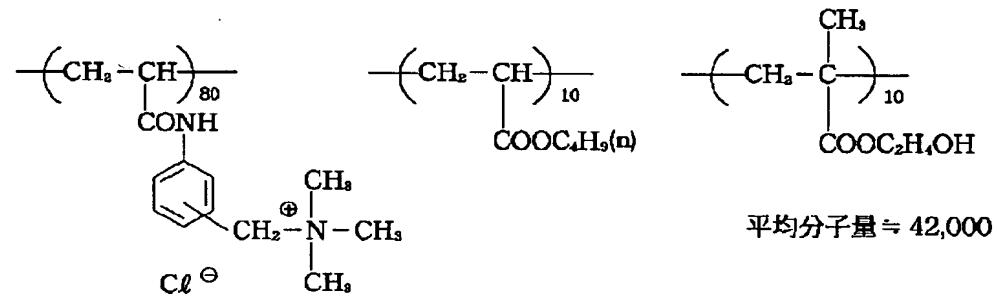


[0104]
[Formula 7]

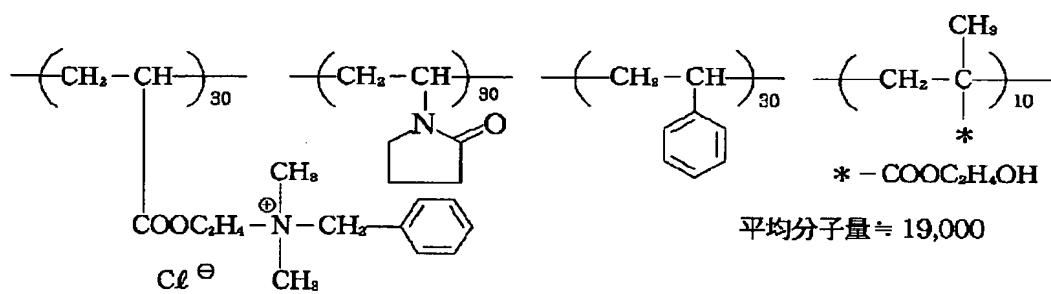
Mor-9



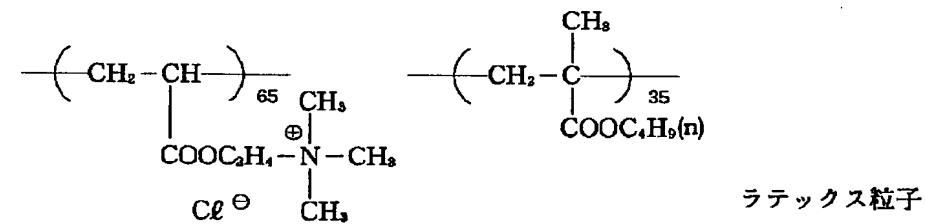
Mor-10



Mor-11



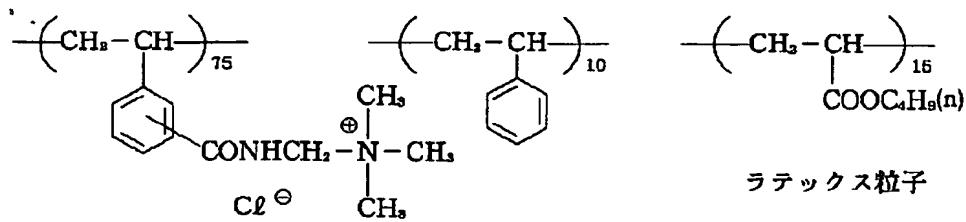
Mor-12



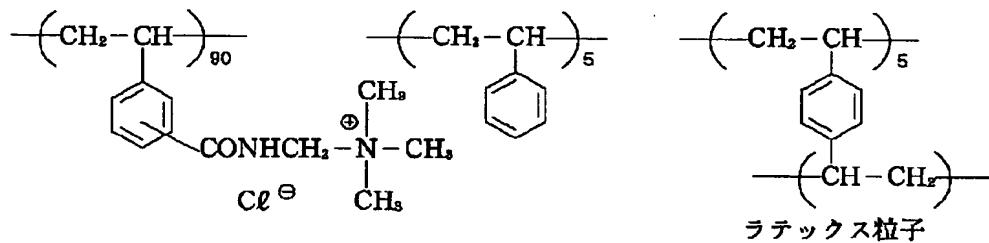
[0105]

[Formula 8]

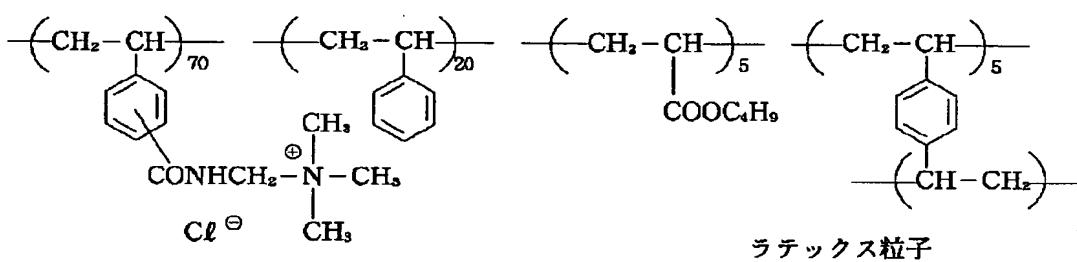
Mor-13



Mor-14



Mor-15



Even if a cation mordant is a polymer mordant which consists of a water-soluble polymer, it may be a polymer mordant which consists of a latex particle compounded by the emulsion polymerization. When an ink absorption layer is an ink absorption layer of a swelling mold and a latex mordant is [an ink absorption layer] an ink absorption layer of an opening mold again, a water-soluble polymer mordant is desirable.

[0106] Since a cation site contributes to a water resisting property or damp-proof amelioration effectively since condensation with a non-subtlety particle has few cation mordants whose mean molecular weights are 50,000 or less, and glossiness cannot deteriorate easily in a water-soluble cation mordant, it is desirable.

[0107] Desirable average molecular weight is 30,000 or less. The minimum of average molecular weight is 2000 or more more nearly about than a water resisting property or a damp-proof viewpoint, although there is especially no constraint.

[0108] A mean molecular weight says the polystyrene reduced property which is the thing of number average molecular weight and was calculated from the gel bar MIESHON chromatography here.

[0109] Although an ink absorption layer changes with concentration, recording density, etc. of a color of recording ink further in absorptivity or non-absorptivity, generally as for the amount of the mordant used, a swelling mold, an opening mold, and 0.2-10g per two of base materials are preferably used for it in 0.5-5g 1m of record forms.

[0110] A record form is an opening mold, when the water-soluble polymer is used as a cation mordant, the ratio of a cation mordant and a non-subtlety particle is important, and it is desirable that the ratios of the cation mordant to a non-subtlety particle are 0.01-0.3 in a weight ratio.

[0111] Curl tends to become a problem, when a water resisting property and damp-proof effectiveness tend to become inadequate and 0.3 is exceeded in the case of less than 0.01.

[0112] In this invention, it is required to make the film surface pH by the side of the recording surface of an ink jet record form into a specific value (3 or more [i.e.,]) and 5 or less range.

[0113] In the record form of this invention, since the film surface pH by the side of the recording surface of an ink jet record form was selected to the specific value, a best water resisting property and best moisture resistance can be acquired by use of the cation mordant of the need minimal dose, the amount of the cation mordant used can be pressed down to the minimum, and it can prevent the defect by abundant use of a cation mordant arising.

[0114] In case ink jet record is carried out although a water resisting property and moisture resistance improve sharply when a film surface pH is less than three, the moment recording ink contacted the record form front face, a color condenses, or a color deposits on a front face by the passage of time after record, the good maximum concentration is not obtained or a poor color tone is caused.

[0115] When a film surface pH exceeds 5, a water resisting property and moisture resistance become inadequate, and a damp-proof fall is especially large.

[0116] When the film surface pH exceeded 5 and it is saved under highly humid after printing, the mobility of a color increased with the moisture incorporated in the ink absorption layer, and although the reason a film surface pH affects moisture resistance is not certain, even if the thione mordant contains, I think that a color will spread.

[0117] The blot after this printing tends to take place by the time of the high-boiling point organic solvent of hydrophilic properties, such as a glycerol and a diethylene glycol, which it is more remarkable to save under highly humid from immediately after printing, and is contained in recording ink having not evaporated from a coat.

[0118] When saved under highly humid, in order for each dot printed with the ink jet printer to pass and to spread in the time, it appears as concentration change especially in the highlights section or a middle concentration region.

[0119] Since it is thought that a film surface pH will change when it dips underwater, the reason a film surface pH affects a water resisting property is not certain, but when a film surface is specific pH, even if a color dyes to a mordant firmly and is dipped underwater, the thing which outflow-comes to be hard is presumed.

[0120] Setting to this invention, a film surface pH is a J.TAPPI paper pulp test method. According to the approach of a publication, the front face pH measured after 30 seconds is said to No.49 using distilled water.

[0121] It is the approach of setting pH of the coating liquid which forms ** ink absorption layer as the value which was able to be decided beforehand as an approach of adjusting a film surface pH to the range of this invention (3 or more [i.e.,]), and 5 or less, and setting to the target pH after spreading desiccation.

** How to carry out the OBAO coat of the liquid of suitable pH, to dry and to acquire the target pH after spreading desiccation of an ink absorption layer.

** How to dip and dry in the water solution of suitable pH after spreading desiccation of an ink absorption layer.**** is mentioned.

[0122] Considering the point that the manufacture approach is simple among the approaches of the above-mentioned ** - **, the approach of ** is desirable.

[0123] ** When enforcing an approach, pH of coating liquid and pH of the film surface of a dry paint film are required in order that asking for pH of coating liquid and relation with a film surface pH by experiment etc. beforehand since it is not necessarily in agreement may make it the target film surface pH.

[0124] Accommodation of a film surface pH is performed combining various kinds of acids or alkali suitably.

[0125] As an acid, organic acids, such as inorganic acids, such as a hydrochloric acid, a nitric acid, a sulfuric acid, and phosphoric acid, an acetic acid, a citric acid, and a succinic acid, are used, and hydroxylation NATORIMU, a potassium hydroxide, a calcium hydroxide, aqueous ammonia, potassium carbonate, a sodium carbonate, trisodium phosphate, triethanolamine, etc. are used as alkali, for example.

[0126] Otherwise in an ink absorption layer, various additives can be added. Hereafter, it explains.

[0127] In the ink absorption layer of the record form of this invention, the hardening agent which can construct a bridge in a hydrophilic binder can be added.

[0128] When an ink absorption layer is an ink absorption layer of a swelling mold, since the rate of absorption of ink falls notably by dura-mater-izing, the amount of the hardening agent used should be made the minimum.

[0129] Since ink rate of absorption is improved by dura-mater-izing when an ink absorption layer is an ink absorption layer of an opening mold, it is desirable to construct a bridge in a hydrophilic binder. Ink rate of absorption is improved by carrying out the dura mater of the hydrophilic binder, because the bloating tendency over the liquid ink of a hydrophilic binder is controlled and lock out of an opening is prevented.

[0130] A hardening agent is a compound which has the various functional groups which the hydrophilic binder has, and the radical which can react, for example, is a compound which has an epoxy group, a formyl group, an ethylene imino group, an activity vinyl group, etc.

[0131] Although the addition of a hardening agent changes greatly with differences in an ink absorption layer like the above, in a swelling mold, it is 5-500mg per hydrophilic binder 1g in 0.1-20mg per hydrophilic binder 1g, and an opening mold.

[0132] In polyvinyl alcohol desirable as a hydrophilic binder used by this invention, it is desirable to add a way acid and/or way sand as a hardening agent. The amount of a way acid and/or the way sand used is 50-500mg per polyvinyl alcohol 1g.

[0133] In addition to the above, for example, an ultraviolet ray absorbent given in JP,57-74193,A, a 57-87988 official report, and a 62-261476 official report, JP,57-74192,A, a 57-87989 official report, a 60-72785 official

report. The fading inhibitor indicated by a 61-146591 official report, JP,1-95091,A, the 3-13376 official report, etc., An anion, a cation or the various surfactants of non-ion, JP,59-42993,A, The fluorescent brightener indicated by a 59-52689 official report, a 62-280069 official report, a 61-242871 official report, JP,4-219266,A, etc., Various well-known additives, such as lubricant, such as a defoaming agent and a diethylene glycol, antiseptics, a thickener, an antistatic agent, and a mat agent, can also be made to contain.

[0134] The ink jet record form of this invention may have the ink absorption layer more than two-layer in the same base material side. In this case, an ink absorption layer may be an ink absorption layer of a swelling mold, or may be an ink absorption layer of an opening mold.

[0135] The following are mentioned as an example of concrete lamination.

** The record form which consists only of the ink absorption layer of an opening mold (the multistory configuration of the ink absorption layer of an opening mold is included.).

** The record form which consists only of the ink absorption layer of a swelling mold (the multistory configuration of the ink absorption layer of a swelling mold is included.).

** The record form which the ink absorption layer of a swelling mold is prepared in a lower layer, and has the ink absorption layer of an opening mold in the upper layer (the case where each layer has become more than two-layer is included.).

** The record form which the ink absorption layer of an opening mold is prepared in a lower layer, and has the ink absorption layer of a swelling mold in the upper layer (the case where each layer has become more than two-layer is included.).

[0136] In the ink jet record form of this invention, in order to adhere at the time of laying on top of the opposite side immediately after curl prevention and printing and to aim at prevention of a ** ink imprint, as for an ink absorption layer, it is desirable to prepare the back layer of various classes.

[0137] Although a back layer changes also with the class of base material, thickness, and the configuration and thickness of an ink absorption layer, generally a hydrophilic binder and a hydrophobic binder are used as a binder. The range of the thickness of a back layer is usually 0.1-10 micrometers.

[0138] Moreover, it can adhere to a back layer as other record forms, and a front face can be split-face-ized to prevention, amelioration of note nature, and a pan for amelioration of the conveyance nature within an ink jet recording device. The organic or inorganic particle whose particle size is 2-20 micrometers can be used for split-face-ization.

[0139] Next, when carrying out ink jet record using the record form of this invention, the aquosity recording ink to be used is explained.

[0140] Aquosity recording ink usually consists of an additive of water soluble dye and a solvent object, and others. Although water soluble dye, such as direct dye used by well-known ink jet record as water soluble dye, acid dye, basic dye, reactive dye, or a food dye, can be used, direct dye or acid dye is desirable.

[0141] Although the solvent of aquosity recording ink makes water a subject, when recording ink dries, a color deposits, and in order to prevent starting blinding in a nozzle tip or an ink supply path, a high-boiling point organic solvent with the boiling point liquefied above about 120 degrees C is usually added at a room temperature. It is required that it should have vapor pressure with far lower required therefore than water having the operation which prevents that formed elements, such as a color, deposit when water evaporates, and a big and rough sludge generates a high-boiling point organic solvent. Moreover, the miscibility over water needs to be high.

[0142] As a high-boiling point organic solvent used for such the purpose For example, ethylene glycol, propylene glycol, a diethylene glycol, Triethylene glycol, a glycerol, the diethylene-glycol monomethyl ether, The diethylene-glycol monobutyl ether, the triethylene glycol monobutyl ether, The glycerol monomethyl ether, 1 and 2, 3-butane triol, 1 and 2, 4-butane triol, 1, 2, 4-** NTAN triol, 1 and 2, 6-hexane triol, thiodiglycol, triethanolamine, a polyethylene glycol (average molecular weight is about 300 or less), etc. are mentioned. Moreover, dimethylformamide, N-methyl pyrrolidone, etc. can be used also besides having described above.

[0143] Also in the high-boiling point organic solvent of these many, the low-grade alkyl ether of polyhydric alcohol, such as polyhydric alcohol, such as a diethylene glycol, triethanolamine, a glycerol, and triethanolamine, and the triethylene glycol monobutyl ether, etc. is desirable.

[0144] As an additive of others which water color ink contains, a pH regulator, a sequestering agent, an antifungal agent, a viscosity controlling agent, a surface tension regulator, a wetting agent, a surfactant, a rust-proofer, etc. are mentioned, for example.

[0145] Water color ink is the purpose which wettability to a record form is made [purpose] good, or stabilizes the regurgitation from an ink jet nozzle, and it is desirable in 25 degrees C to have the surface tension of 28 - 40 dyne/cm within the limits preferably 25 to 50 dyne/cm.

[0146] Moreover, in 25 degrees C, 2 - 10cp is desirable still more desirable, and the viscosity of water color ink is usually 2.5 - 8cp.

[0147] In the ink jet record approach of this invention, it is desirable in the effectiveness of this invention to

make pH of recording ink into 3 or more and 8 or less to that of the maximum *****.

[0148] By making pH of recording ink or less into eight, it is recorded in the environment where relative humidity exceeds 80% especially when it combines with the ink jet record form of this invention, and when saved in the condition as it is, the amelioration effectiveness over moisture resistance becomes large.

[0149] If pH of recording ink becomes less than three, the stability of water soluble dye falls, and it will become or will become easy to corrode for blinding a lifting and the quality of the material of the various kinds in the ink liquid supply path in an ink jet printer which becomes empty.

[0150] Furthermore, pH of desirable recording ink is 3.5-7.

[0151] When the capacity of the liquid ink drop breathed out from an ink nozzle is 1-30pL, since the diameter of a dot with a diameter of about 20-60 micrometers is obtained in the record paper, it is desirable. The color-print printed with such a diameter of a dot gives a high-definition image. Furthermore, the capacity of a desirable liquid ink drop is 2-20pL.

[0152] Moreover, at least, when carrying out ink jet record by the recording method using the aquosity recording ink which is two kinds from which concentration differs more than twice in a Magenta and cyanogen, since low-concentration ink is used, it is hard coming to carry out discernment of a dot in the highlights section, but also when this recording method is used, these faults do not produce this invention.

[0153] In the ink jet record approach, various kinds of well-known methods can be conventionally used as the record approach. The detail of the record approach is indicated by the trend (the volume for Koichi Nakamura, March 31, Heisei 7, the Japan science-information incorporated company issue) of for example, an ink jet record technique.

[0154]

[Example] This invention is not limited by these examples although an example explains this invention concretely below.

[0155] The paper base material which covered both sides of 1160g of examples/, and the stencil paper for photographs of m2 with polyethylene (the polyethylene layer which contains an anatase mold titanium dioxide with a thickness of 35 micrometers 13% of the weight is formed in the recording surface side.) As for thickness, a polyethylene layer is formed in a rear-face side by 25 micrometers, and the back layer which makes a mat agent the silica 0.6 g/m2 and whose mean diameter are about 13 micrometers, and contains it two times 0.3 g/m is formed on it by making Tg=65 degree C acrylic latex resin into solid content. It prepared.

<Production of coating liquid 1-1> In 900ml of pure water, it added, while the mean diameter of a primary particle agitated 180g of particle silica powder compounded by the gaseous-phase method which is about 7nm with the high-speed homogenizer, and the silica water dispersion was produced. Next, in this silica water dispersion, 100ml of 25% water solutions of instantiation mordant Mor-1 (cation mordant) was added, the high-speed homogenizer distributed for 30 minutes, and pale clear dispersion liquid were obtained. Next, average degree of polymerization added 1ml of 10% polyvinyl alcohol water solutions whenever [saponification / whose] is 88% by 300, and average degree of polymerization added gradually further 530ml (ethyl acetate is contained 4% of the weight) of 5% polyvinyl alcohol water solutions whenever [saponification / whose] is 88% by 3500. Subsequently, 40ml of borated water solutions was added 4% as a hardening agent, and 20ml ethanol was added, and the coating liquid 1-1 which adds 50ml of gelatin water solutions 10%, and forms the ink absorption layer of an opening mold further was produced.

<Production of the record form 1-1> The coating liquid 1-1 warmed at 40 degrees C was applied so that humid thickness might be set to 260 micrometers at the recording surface side of the paper base material which covered above-mentioned both sides with polyethylene, and it cooled so that spreading coat temperature might become 15 degrees C or less (for 20 seconds). Subsequently, the 40-degree C wind was sprayed for the 30-degree C wind for 60 seconds for 60 seconds, for 120 seconds and a 35 more-degree C wind were sprayed for 60 seconds and for a 50-degree C wind one by one for 60 seconds, the 25-degree C wind was dried, further, 25 degrees C and the ambient atmosphere of 50% of relative humidity were passed for 120 seconds, gas conditioning was carried out, and the record form 1-1 was produced.

[0156] The film surface pH of the obtained record form 1-1 is shown in Table 1.

<Production of the record form 1-2 to 1-5> pH of coating liquid 1-1 was changed using the nitric acid or the sodium hydroxide, and the record form 1-2 to 1-5 as well as the record form 1-1 was produced.

[0157] The film surface pH of the obtained record form 1-2 to 1-5 is shown in Table 1.

[0158] About the obtained record form 1-1 to 1-5, void volume, ink absorptivity, glossiness, curl, a water resisting property, moisture resistance, lightfastness, and maximum density were evaluated by the following.

1 Void volume Kumagaya Riki Kogyo K.K. make and a Bristow testing-machine II mold (pressure type) were used, and the amount of transition for [contact time] 2 seconds (ml/m2) was calculated as void volume.

2 Ink absorptivity Kumagaya Riki Kogyo K.K. make and a Bristow testing-machine II mold (pressure type) were used, and contact time calculated ink absorptivity from the amount of transition in 0.5 seconds (ml/m2).

3 The specular gloss was measured 75 degrees with the deflection photometer (VGS-101DP) by glossiness

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4 The sample of A5 size was left for 30 minutes by the environment where curl 23degree C and relative humidity are 20%, and the environment where 30 degrees C and relative humidity are 80%, and the height of four corners was measured by them, they were asked for the average, and curl was evaluated by them. When a recording surface was turned up, a record form was laid on a base, the edge of a record form was higher than the base top, + and a recording surface were turned down, a record form was laid on a base, and the edge of a record form was higher than the base top, the height of curl was displayed as -. If there is this height by **10mm or less, it will be satisfactory in general practically.

[0159] **5** The on-demand mold ink jet printer was used for the waterproof record form, and it printed so that reflection density might be set to about 1.0 with the recording ink of the Magenta ink of the following presentation. After printing, after being immersed into pure water at the room temperature for 12 hours, reflection density was measured again.

[0160] The survival rate of the reflection density after immersion was searched for from the reflection density before being immersed in pure water, and it considered as the water resisting property.
(Presentation of the recording ink of Magenta ink)

Pure water 75ml Diethylene glycol 10.3g Glycerol 7.3g C9H19O(CH₂OCH₂O)10H 0.05g DirectRed227 After 1.7g sodium hydroxide / sulfuric acid adjusts to pH=5.0**0.1, 100ml is made with pure water.

6 The on-demand mold ink jet printer was used for the damp-proof record form under 23 degrees C and the environment of 80% of relative humidity, and it printed so that reflection density might be set to about 0.5 with the recording ink of the Magenta ink of the above-mentioned presentation. It was left in the state of [as it is] after printing for 48 hours. The rate of change (with no concentration change of 0%) of the reflection density after the neglect to the reflection density immediately after printing was investigated, and it considered as moisture resistance.

7 The on-demand mold ink jet printer was used for the light-fast record form, and it printed so that reflection density might be set to about 1.0 with the recording ink of the Magenta ink of the above-mentioned presentation. The reflection density after 100-hour Mitsuteru putting and an optical exposure was measured in the printed record form using xenon fade meter, and it asked for the ratio of the reflection density after the optical exposure to the reflection density before an optical exposure as a coloring matter survival rate, and considered as lightfastness.

8 The on-demand mold ink jet printer was used for the maximum-density record form, it printed on the conditions from which the maximum density of a Magenta is obtained with the recording ink of the Magenta ink of the following presentation, the reflection density was measured, and it considered as maximum density.

[0161] The above result was shown in Table 1.

[0162]

[Table 1]

記録用紙	膜面pH	空隙容量	インク吸収性	光沢度	カール (mm)		耐水性 (%)	耐湿性 (%)	耐光性 (%)	最大濃度
					23°C/20%	30°C/80%				
1-1 比較例	5.5	38.0	24.0	62.0	+3.0	-3.0	83.4	+25	72	2.09
1-2 本発明	4.5	37.5	24.5	62.7	+3.0	-2.5	89.6	+7	70	2.04
1-3 本発明	4.0	37.5	23.5	63.3	+3.5	-3.0	90.4	+4	70	2.05
1-4 本発明	3.5	37.0	23.0	61.8	+2.5	-2.0	92.2	+2	69	2.00
1-5 比較例	2.5	37.5	23.5	63.6	+2.5	-3.0	95.3	+2	63	1.73

[0163] The result of Table 1 shows improving both moisture resistance and a water resisting property, without the record form 1-2 to 1-4 which adjusted the film surface pH to the range of 3-5 almost having a bad influence on void volume, ink absorptivity, glossiness, curl, and lightfastness.

[0164] On the other hand, the record form 1-1 whose film surface pH is 5.5 is inferior, although a water resisting property is low a little and especially moisture resistance contains the cation mordant. Moreover, the remarkable fall of the maximum concentration expected to follow a water resisting property and moisture resistance on crystallization of a color although the record form 1-5 which set the film surface pH to 2.5 is excellent is accepted.

[0165] The record form 2-1 to 2-5 which has the film surface pH which shows example-2 instantiation mordant Mor-1 for an instantiation mordant in Table 2 like an example -1 except having changed into Mor-4 was produced. About the obtained record form 2-1 to 2-5, void volume, ink absorptivity, glossiness, curl, a water resisting property, moisture resistance, lightfastness, and maximum density were evaluated like the example -1. The obtained result is shown in Table 2.

[0166].
[Table 2]

記録用紙		膜面pH	空隙容量	インク吸収性	光沢度	カール (mm)		耐水性 (%)	耐湿性 (%)	耐光性 (%)	最大濃度
						23°C/20%	30°C/80%				
2-1	比較例	5.7	39.0	26.0	63.6	+6.5	-5.0	86.2	+22	70	2.02
2-2	本発明	4.8	38.5	26.5	64.1	+7.0	-5.5	91.2	+6	69	2.01
2-3	本発明	4.2	38.0	25.5	64.3	+7.5	-6.5	94.4	+2	68	2.01
2-4	本発明	3.7	38.5	26.0	63.7	+6.5	-5.0	96.2	+2	68	1.97
2-5	比較例	2.6	38.5	24.5	64.2	+7.5	-6.5	97.3	+2	64	1.65

[0167] Also when a cation mordant is changed into instantiation mordant Mor-4 which are a cation monomer homopolymer from the result of Table 2, it turns out that the same effectiveness as an example -1 is acquired.

[0168] Although a curl property falls a little as compared with instantiation mordant Mor-1 when instantiation mordant Mor-4 are used, a water resisting property and moisture resistance are improving.

[0169] While the mean particle diameter of an example-3 <production of coating liquid 3-1> primary particle added 100ml of pure water to 900ml of 20% colloidal silica water solutions which are about 20nm and agitated with the high-speed homogenizer, 150ml of 25% water solutions of instantiation mordant Mor-1 was added, the high-speed homogenizer distributed for 30 more minutes, and pale clear dispersion liquid were obtained. Next, average degree of polymerization added 2ml for 10% polyvinyl alcohol water solution whenever [saponification / whose] is 88% by 300, and average degree of polymerization added gradually further 650ml (ethyl acetate is contained 4% of the weight) of 5% polyvinyl alcohol water solutions whenever [saponification / whose] is 88% by 3500. Subsequently, 40ml of borated water solutions was added 4% as a hardening agent, and 20ml ethanol was added, and the coating liquid 3-1 which adds 50ml of gelatin water solutions 10%, and forms the ink absorption layer of an opening mold further was produced.

<Production of the record form 3-1 to 3-5> Using the above-mentioned coating liquid 3-1, like the example -1, it dried and the record form 3-1 which has spreading and the film surface pH shown in Table 3 was produced on the base material used in the example -1. Furthermore, the record form 3-2 to 3-5 to which the film surface pH was changed like the example -1 so that it might become as [show / in Table 3] was produced.

[0170] About the obtained record form 3-1 to 3-5, void volume, ink absorptivity, glossiness, curl, a water resisting property, moisture resistance, lightfastness, and maximum density were evaluated like the example -1. The obtained result is shown in Table 3.

[0171]

[Table 3]

記録用紙		膜面pH	空隙容量	インク吸収性	光沢度	カール (mm)		耐水性 (%)	耐湿性 (%)	耐光性 (%)	最大濃度
						23°C/20%	30°C/80%				
3-1	比較例	5.4	31.0	19.5	57.3	+3.5	-3.5	80.1	+32	62	2.17
3-2	本発明	4.8	31.5	20.0	58.3	+3.0	-3.5	86.2	+9	61	2.15
3-3	本発明	4.1	32.0	20.0	57.8	+3.5	-3.5	88.3	+6	61	2.15
3-4	本発明	3.5	31.5	19.5	57.4	+2.5	-4.0	89.5	+4	63	2.13
3-5	比較例	2.5	31.0	19.5	57.2	+3.5	-3.5	90.7	+4	62	1.82

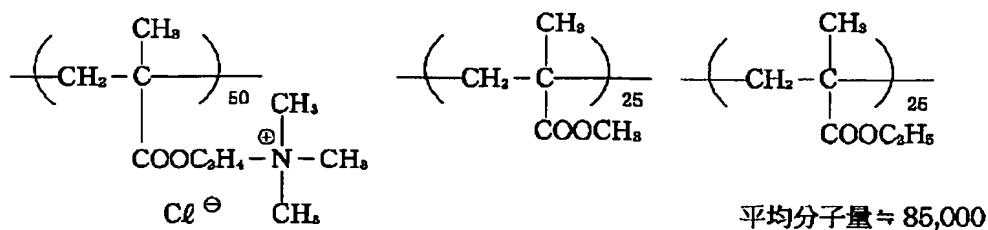
[0172] Although void volume falls when it replaces with the silica compounded by the gaseous-phase method and colloidal silica is used from the result shown in Table 3, it turns out that a water resisting property and moisture resistance are improved without the record form 3-2 to 3-4 which set the film surface pH to 3-5 like the example -1 reducing the maximum concentration.

[0173] It replaced with the particle silica powder compounded by the gaseous-phase method the mean particle diameter of a 41st [-] example particle is about 7nm, and the record form 4-1 to 4-3 as well as the record form 1-3 of an example -1 was produced except having used the particle silica powder compounded by the gaseous-phase method the mean particle diameter of a primary particle is 12nm, 20nm, and 50nm.

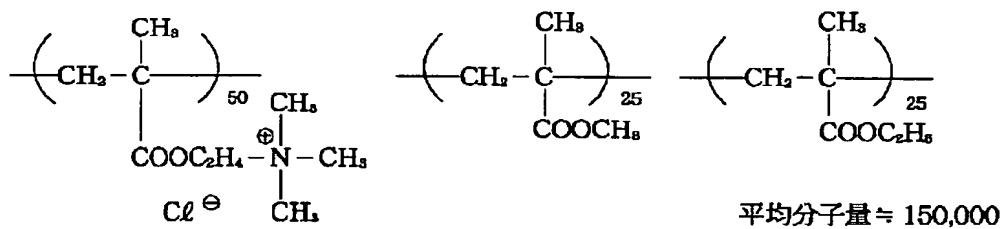
[0174] Moreover, it is the following mordant about instantiation mordant Mor-1. - The record form 4-4 and 4-5 were produced like the record form 1-3 of an example -1 except having changed into A and -B.

[0175]

[Formula 9]
媒染剤 - A



媒染剤 - B



The film surface pH of the obtained record form 4-1 to 4-5 is shown in Table 4.

[0176] Moreover, void volume, ink absorptivity, glossiness, curl, a water resisting property, moisture resistance, lightfastness, and maximum density were evaluated like the example -1 about the obtained record form 4-1 to 4-5. The obtained result is shown in Table 4.

[0177]

[Table 4]

記録用紙		膜面pH	空隙容量	インク吸収性	光沢度	カール (mm)		耐水性 (%)	耐湿性 (%)	耐光性 (%)	最大密度
						23°C/20%	30°C/80%				
4-1	本発明	4.1	36.5	22.0	62.7	+3.5	-3.5	91.3	+6	71	2.03
4-2	本発明	4.0	35.0	22.5	59.2	+2.0	-3.0	93.7	+4	70	2.01
4-3	本発明	4.1	32.0	21.5	48.2	+2.0	-3.5	95.2	+4	68	1.96
4-4	本発明	4.0	37.5	24.5	42.3	+3.5	-4.0	92.5	+4	70	2.01
4-5	本発明	4.1	38.5	23.0	31.4	+3.0	-3.0	93.1	+4	68	1.99

[0178] As shown in Table 4, it has a high water resisting property and high moisture resistance, without neither of the record form 4-1 to 4-5 reducing curl, lightfastness, and the maximum concentration.

[0179] Moreover, if the mean particle diameter of the primary particle of the particle silica powder compounded by the gaseous-phase method increases, void volume and glossiness will fall gradually, and it turns out that the mean particle diameter of the primary particle of a desirable silica is about 30nm or less.

[0180] Moreover, when what has molecular weight high as a mordant is used, it turns out that gloss falls gradually. The minute aggregate has occurred in the coating liquid used for producing the record form 4-4 and 4-5, and this caused the gloss fall.

[0181] The record form 5-1 to 5-4 as well as the record form 1-3 of an example -1 was produced except having changed the ratio of the particle silica (silica) compounded by the example-5 gaseous-phase method, and polyvinyl alcohol (PVA), as shown in Table 5.

[0182] The film surface pH of the obtained record form 5-1 to 5-4 is shown in Table 4.

[0183] Moreover, void volume, ink absorptivity, glossiness, curl, a water resisting property, moisture resistance, lightfastness, and maximum density were evaluated like the example -1 about the obtained record form 5-1 to 5-4. The obtained result is shown in Table 5.

[0184] Moreover, the film surface pH of the record form 1-3, void volume, ink absorptivity, glossiness, curl, a water resisting property, moisture resistance, lightfastness, and maximum density were shown in Table 5 for reference.

[0185]

[Table 5]

記録用紙		(シリカ/PVA)比	膜面pH	空隙容量	インク吸収性	光沢度	カール (mm)		耐水性 (%)	耐湿性 (%)	耐光性 (%)	最大温度
							23°C/20%	30°C/80%				
1-3	本発明	7.2	4.0	37.5	23.5	63.3	+3.5	-3.0	90.4	+4	70	2.05
5-1	本発明	10.5	3.9	40.5	28.5	42.2	+5.0	-5.5	93.2	+7	64	1.97
5-2	本発明	5.0	4.0	34.5	19.5	66.5	+3.0	-2.0	89.3	+4	72	2.05
5-3	本発明	3.0	4.1	31.0	14.0	69.2	+2.0	-1.5	87.4	+4	74	2.09
5-4	本発明	1.5	4.0	23.0	10.5	73.2	+2.0	-1.5	86.3	+4	78	2.11

[0186] As shown in Table 5, it has a high water resisting property and high moisture resistance, without neither of the record form 5-1 to 5-4 reducing curl, lightfastness, and the maximum concentration.

[0187] Although void volume becomes large and ink absorptivity is improved, a minute crack generates the record form 5-1 which made ten or more the ratio to the polyvinyl alcohol of the particle silica powder compounded by the gaseous-phase method on the whole surface, and gloss is falling. Moreover, void volume is falling in the record form 5-4 which made two or less the ratio to the polyvinyl alcohol of the particle silica powder compounded by the gaseous-phase method.

[0188] The coating liquid 6-1 containing the component below per [example-6 <production of coating liquid 6-1> coating liquid 1L] was produced.

[0189]

Acid-treatment gelatin 38g Polyvinyl pyrrolidone (K-90) 12g Polyethylene oxide (average molecular weight = about 150,000) 10g Mordant (instantiation mordant Mor-15) 32g Cationic fluorescent brightener 0.1g Hardening agent (H-1) : (H-1) pentane [1 and 5-diglycidyl-3-hydroxy] <production of the record form 6-1> 0.2g the obtained coating liquid 6-1 The paper base material which covered both sides of 150g/the stencil paper for photographs of m2 with polyethylene (the polyethylene layer which contains an anatase mold titanium dioxide with a thickness of 35 micrometers 13% of the weight is formed in the recording surface side) A polyethylene layer with a thickness of 25 micrometers should be formed in a rear-face side, and let on it the silica gelatin 2.2g and whose mean particle diameter are about 2 micrometers be a mat agent. The back layer contained two times 0.1 g/m is formed. After applying and carrying out a cooling set so that humid thickness may turn to 120 micrometers at a recording surface side, it dried and the record form 6-1 was obtained.

[0190] The film surface pH of the obtained record form 6-1 is shown in Table 6.

<Production of the record form 6-2 to 6-5> pH of coating liquid 6-1 was changed using the nitric acid or the sodium hydroxide, and the record form 6-2 to 6-5 as well as the record form 6-1 was produced.

[0191] The film surface pH of the obtained record form 6-2 to 6-5 is shown in Table 6.

[0192] Moreover, glossiness, curl, a water resisting property, moisture resistance, lightfastness, and maximum density were evaluated like the example -1 about the obtained record form 6-1 to 6-5. The obtained result is shown in Table 6.

[0193]

[Table 6]

記録用紙		膜面pH	光沢度	カール (mm)		耐水性 (%)	耐湿性 (%)	耐光性 (%)	最大温度
				23°C/20%	30°C/80%				
6-1	比較例	5.4	62.0	+8.0	-6.0	84.7	+19	79	2.12
6-2	本発明	4.8	62.7	+7.5	-6.5	87.1	+8	77	2.13
6-3	本発明	4.1	63.3	+9.0	-7.0	89.2	+4	78	2.15
6-4	本発明	3.6	61.8	+8.5	-6.5	90.5	+4	77	2.12
6-5	比較例	2.5	63.6	+8.5	-7.0	92.1	+2	76	1.53

The result of Table 6 shows that the same effectiveness as the ink absorption layer of an opening mold is acquired even if it is the case where an ink absorption layer is a swelling mold.

[0194] Except that the amount of example-of comparison 1 instantiation mordant Mor-1 is changed as shown in Table 7, and it was made for a film surface pH to come to show in Table 7, the record form 7-1 to 7-3 as well as the record form 1-1 of an example -1 was produced. In addition, it was made for the coverage of the particle silica powder compounded by the gaseous-phase method and polyvinyl alcohol to become fixed. Therefore, it follows on making the amount of instantiation mordant Mor-1 increase, and thickness is thick.

[0195] The film surface pH of the obtained record form 7-1 to 7-3 is shown in Table 7.

[0196] About the obtained record form 7-1 to 7-3, void volume, ink absorptivity, glossiness, curl, a water resisting property, moisture resistance, lightfastness, and maximum density were evaluated like the example -1. The obtained result is shown in Table 7.

[0197] Moreover, the amount of mordants of the record form 1-1, a film surface pH, void volume, ink absorptivity, glossiness, curl, a water resisting property, moisture resistance, lightfastness, and maximum density were shown in Table 7 for reference.

[0198]

[Table 7]

記録用紙		媒染剂量 (ml)	膜面 pH	空隙容量	インク 吸収性	光沢度	カール (mm)		耐水性 (%)	耐湿性 (%)	耐光性 (%)	最大濃度
							23°C/20%	30°C/80%				
1-1	比較例	100	5.5	38.0	24.0	62.0	+3.0	-3.0	83.4	+25	72	2.09
7-1	比較例	150	5.6	36.5	22.5	63.2	+9.5	-6.5	87.0	+21	60	2.08
7-2	比較例	200	5.6	36.0	20.5	63.7	+14.5	-10.0	91.3	+15	51	2.06
7-3	比較例	300	5.7	32.5	18.0	64.1	+21.0	-15.0	92.2	+11	37	2.08

[0199] As shown in Table 7, even when a film surface pH is five or more, if the quantity of the amount of a cation mordant is increased, a water resisting property and moisture resistance will improve greatly, but when it is made five or less film surface pH, moisture resistance cannot be improved to like. Moreover, if the quantity of the amount of a cation mordant is increased, curl will become large and lightfastness will get worse rapidly.

[0200]

[Effect of the Invention] The ink jet record form of this invention can attain the water resisting property and moisture resistance with the at least sufficiently high amount used of a cation mordant, and can press down bad influences, such as increase of curl brought about by use of a cation mordant, light-fast low-izing, and contamination, to the minimum.

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PRIOR ART

[Description of the Prior Art] although ink jet record makes the minute drop of ink fly by various working principles, and is made to adhere to record sheets, such as paper, and an image, an alphabetic character, etc. are recorded, a high speed, the low noise, and multiple-colorizing are comparatively easy — etc. — it has the advantage. About the blinding of a nozzle and the maintenance which had become a problem from the former by this method, from both sides of ink and equipment, amelioration progresses and it has spread quickly in various fields, such as various printers, facsimile, and a computer terminal, in current.

[0003] The detail is indicated by the trend (the volume for Koichi Nakamura, March 31, Heisei 7, the Japan science-information incorporated company issue) of for example, an ink jet record technique.

[0004] As a record form used by this ink jet recording method, also when a printing dot laps [that a color tone is brightly skillful and absorption of ink] early, the diffusion to the longitudinal direction of ink flowing out or not spreading and a printing dot is not large [the concentration of a printing dot is high, and] beyond the need, and generally it is required that the circumference should be smooth and should not fade etc.

[0005] As an ink jet record form, various record forms are used from the former. For example, the ink jet record form which painted the ink absorption layer as a record layer on the base material which consists of a regular paper, a hydrophilic binder and various kinds of coated paper which painted the layer which consists of an inorganic pigment (art paper, coat paper, cast coated paper, etc.), various kinds of papers that covered both sides with plastic resin, transparency, or various kinds of opaque plastic film is used further.

[0006] The above-mentioned ink absorption layer is roughly divided into the ink absorption layer of the opening mold which prepared the opening into the ink absorption layer of the swelling mold constituted by the subject in the hydrophilic binder, and the record layer.

[0007] The ink absorption layer of a swelling mold holds ink in a swelling operation of a hydrophilic binder. As a hydrophilic binder, for example Gelatin, polyvinyl alcohol, Polyethylene oxide, a polyvinyl pyrrolidone, a pullulan, a carboxymethyl cellulose, Hydroxyethyl cellulose, a dextran, a dextrin, polyacrylic acid, and its salt, An agar, a kappa carrageenan, lambda-carrageenan, iota-carrageenan, xanthene gum, A polyalkylene oxide system copolymerization polymer given in locust bean gum, an alginic acid, gum arabic, JP,7-195826,A, and a 7-9757 official report, A homopolymer, a copolymer, etc. of the vinyl monomer which has a water-soluble polyvinyl butyral, or a carboxyl group and a sulfonic group given in JP,62-245260,A are independent, or are used combining two or more sorts.

[0008] The ink absorption layer of an opening mold holds ink to the opening formed in the layer, and the opening is usually formed by making various kinds of inorganic solid-state particles and organic solid-state particles contain in a coat.

[0009] If a non-subtlety particle is used and carried out for the above-mentioned purpose, white inorganic pigments, such as precipitated calcium carbonate, whiting, a magnesium carbonate, a kaolin, clay, talc, a calcium sulfate, a barium sulfate, a titanium dioxide, a zinc oxide, zinc hydroxide, zinc sulfide, zinc carbonate, a hydrotalcite, aluminum silicate, the diatom earth, a calcium silicate, a magnesium silicate, synthetic amorphous silica, colloidal silica, an alumina, a colloidal alumina, pseudo-boehmite, an aluminum hydroxide, a lithopone, a zeolite, and a magnesium hydroxide, etc. are mentioned, for example

[0010] Even if it distributes homogeneity in a binder with a primary particle, these non-subtlety particles may form secondary floc, and homogeneity may be made to distribute them in a binder.

[0011] As an organic particle, particles, such as polystyrene, polyacrylic ester, polymethacrylic acid ester, polyacrylamides, polyethylene, polypropylene, a polyvinyl chloride, polyvinylidene chlorides or these copolymers, a urea-resin, and melamine resin, are mentioned, for example.

[0012] In the ink jet recording method, although the color picture of high saturation is obtained when a water-soluble color is used for recording ink, a water resisting property and moisture resistance are inferior. on the other hand — although it excels a water resisting property and in respect of moisture resistance when a pigment is used for recording ink — the spectral extinction property of color material — broadcloth ** — the coloring matter image of high saturation is hard to be obtained.

[0013] In order to improve the water resisting property and moisture resistance at the time of using the

recording ink which used the water-soluble color which is inferior in a water resisting property or moisture resistance, the various approaches to which coloring matter is made to fix from the former are proposed.

[0014] An effective means to improve a water resisting property and moisture resistance in these proposals is an approach using the uniform water solution and particle latex of a cationic polymer which have the nitrogen atom of the 3rd class or the 4th class.

[0015] As the former and ink jet recording method or an ink jet record form, To JP,57-36692,A, for example, on stencil paper or a polyethylene terephthalate film base material The ink jet record form which painted the coating liquid containing gelatin and a basic mordant, and was used as the ink absorbing layer The water-color-ink record form which infiltrated polyethyleneimine into paper in JP,53-49113,A The record material which has the electrolyte polymer which has a cation or an anion radical in JP,58-24492,A In JP,63-224988,A, the 1st class thru/or tertiary amine, or quarternary ammonium salt is contained. The charge of a recorded material which has the ink absorbing layer which set pH to 2-8 to JP,63-307979,A The ink jet record sheet which prepared the layer containing the polymer which has the hydrophilic polymer mordant which has the 3rd class or the 4th class nitrogen atom, and a hydrophilic radical In JP,59-198186,A and a 59-198188 official report The charge of a recorded material which made the organic base of polyethyleneimine contain in the coating layer in a base material or on a base material The method of the ink jet recording method using the ink which contains a specific color in JP,60-46288,A, and the record ingredient containing polyamine etc. In JP,61-61887,A, a 61-72581 official report, a 61-252189 official report, and a 62-174184 official report The ink jet record form containing the poly allylamine to JP,61-172786,A the polymer which has an intermolecular hydrogen bridge, and the polymer (a polyethylene glycol —) which does not have a hydrogen bond nature machine among molecules (gelatin, polyethylene RENIMIN, etc.) The ink jet record ingredient which has a layer containing a polyvinyl pyrrolidone etc. The ink jet record form which applies or infiltrated the cationic polymer and the cationic surface active agent on the base material in JP,63-162275,A The record sheet which has the color fixing layer which uses a quarternary-ammonium-salt polymerization object and cation conversion polyvinyl alcohol as a principal component on a plastics base material, and the color transparency and ink absorption layer which were prepared on it is indicated by JP,6-143798,A.

[0016] Furthermore, JP,59-20696,A, a 59-33176 official report, A 59-33177 official report, a 59-96987 official report, a 59-155088 official report, A 60-11389 official report, a 60-49990 official report, a 60-83882 official report, A 60-109894 official report, a 61-277484 official report, a 61-293886 official report, A 62-19483 official report, a 62-198493 official report, a 63-49478 official report, A 63-115780 official report, a 63-203896 official report, a 63-274583 official report, A 63-280681 official report, a 63-260477 official report, JP,1-9776,A, The nitrogen atom of the 3rd class or the 4th class of specification [a 1-24784 official report, a 1-40371 official report, a 3-133686 official report, a 6-234268 official report, and a 7-125411 official report] Adding the polymer or compound which it has all over an ink absorbing layer is indicated.

[0017] Although the technique which fixes the color indicated by this advanced technology can accept appropriate effectiveness from the point of immobilization of a color, it is not necessarily enough.

[0018] Although what is necessary is just to increase the amount of the mordant used in order to raise a water resisting property and moisture resistance using a cationic mordant, it is easy to produce the various faults accompanying increase in quantity of a cation mordant in this case.

[0019] For example, a cation mordant degrades the lightfastness of the color after record, or a lifting and a cone inclination are during preservation about yellow coloring, and such a fault tends to become remarkable with increase of the addition of a mordant.

[0020] Furthermore, when a water-soluble mordant is used as a cation mordant, there is a fault of making curl increasing, degrading the film formation nature of a coat, or bringing about brittleness with increase of an addition. If the latter problem is large and the addition of a mordant makes it increase especially when an ink absorption layer is the thing of a swelling mold, compatibility with other hydrophilic binders will get worse, and film formation nature and brittleness will be degraded. Moreover, when an ink absorption layer is the thing of an opening mold, in order to have to use an opening layer as a thick film, the addition of a mordant increases and it becomes easy to produce curl.

[0021] Moreover, by becoming easy to produce devitrification and sticking of a coat with increase of an addition, when the latex particle by which the emulsion polymerization was carried out as a cation mordant is used and an ink absorption layer is the thing of a swelling mold, when an ink absorption layer is the thing of an opening mold, an opening will be taken up and void volume will be reduced.

[0022] When the above-mentioned trouble was examined, it became clear that it was solvable by making the pH value of the film surface by the side of the recording surface of an ink absorption layer into a specific value.

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EFFECT OF THE INVENTION

[Effect of the Invention] The ink jet record form of this invention can attain the water resisting property and moisture resistance with the at least sufficiently high amount used of a cation mordant, and can press down bad influences, such as increase of curl brought about by use of a cation mordant, light-fast low-izing, and contamination, to the minimum.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] This invention is made in view of the above-mentioned actual condition, and the 1st purpose of this invention is to offer the ink jet record form which can attain a high water resisting property and high moisture resistance by the amount of few cation mordants used. The 2nd purpose is to offer the ink jet record form which controlled the aforementioned various faults brought about by use of a cation mordant.

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MEANS

[Means for Solving the Problem] The above-mentioned purpose of this invention is an ink jet record form characterized by having at least one layer of ink absorption layers containing the cation mordant which has mordacity to (1) hydrophilic-property binder and an anionic color on a base material, and making the film surface pH by the side of the recording surface of an ink absorption layer into 3 or more and 5 or less.

(2) An ink jet record form given in the above (1) characterized by for the mean particle diameter of a primary particle containing [an ink absorption layer] a non-subtlety particle 30nm or less, and forming the opening.

(3) Ink jet record form given in the above (2) characterized by non-subtlety particles being at least one sort of non-subtlety particles chosen from the silica compounded by the gaseous-phase method, colloidal silica, an alumina, and hydrated alumina.

(4) An ink jet record form given in either of above-mentioned (1) – (3) to which a cation mordant is characterized by average molecular weight being 50,000 or less water-soluble mordant.

(5) An ink jet record form given in either of above-mentioned (1) – (4) to which the amount of a cation mordant is characterized by being 0.01–0.3 in a weight ratio to a non-subtlety particle.

(6) An ink jet record form given in either of above-mentioned (1) – (5) to which a hydrophilic binder is characterized by being polyvinyl alcohol.

(7) An ink jet record form given in the above (6) characterized by an ink absorption layer containing a way acid or way sand.

(8) An ink jet record form given in either of above-mentioned (1) – (7) to which a base material is characterized by being a non-absorptivity base material.

(9) The above (1) The ink jet record approach that pH is characterized by what is recorded with the recording ink it is [recording ink] 3 or more and 8 or less at an ink jet record form given in either of – (8).

It is alike and is attained more.

[0025] Although the recorded material which controlled generating of the odor accompanying a mordant by containing the 1st class – tertiary amine, or quarternary ammonium salt, and adjusting pH of an ink absorbing layer within the limits of 2–8 is previously indicated by JP,63-224988,A shown as advanced technology, it is not indicated by by making the film surface pH by the side of the recording surface of an ink absorption layer into a specific pH value that a water resisting property and moisture resistance are acquired. Moreover, the example which made the film surface pH by the side of the recording surface of an ink absorption layer the range of 3–5 is not indicated by this official report, either, but there is also no publication which suggests selecting the range of 3–5 which were specified as a film surface pH in it. And even if pH of an ink absorbing layer is in the range of 2–8, when the film surfaces pH by the side of the recording surface of an ink absorption layer are not 3–5, the effectiveness of this invention is not acquired.

[0026] Therefore, as for this invention, the above-mentioned advanced technology differs in the purpose, and, moreover, configurations also differ.

[0027] Hereafter, this invention is explained to a detail.

[0028] In this invention, paper base materials, such as the base material used for an ink jet record form from the former, for example, a regular paper, art paper, coat paper, and cast coated paper, a plastics base material, the paper base material that covered both sides with polyolefine, and the compound base material which stuck these can be used as a base material.

[0029] When you wish to obtain the high smooth nature and the maximum density after high glossiness and record, it is desirable to use a non-absorptivity base material. The paper base material which covered both sides with the base material or polyolefine which consists of plastic film as a non-absorptivity base material is used preferably, and the paper base material which covered both sides with polyolefine is used as most desirable thing.

[0030] As a base material which consists of plastic film, the base material which consists of plastic film, such as a polyethylene film, a polypropylene film, a polystyrene film, a polyethylene terephthalate film, a polyethylenenaphthalate film, a triacetyl cellulose film, a polyvinyl chloride film, a polyimide film, a polycarbonate film, and cellophane, is used preferably, for example.

[0031] These plastic film can use suitably a transparent thing, a translucent thing, and an opaque thing properly according to an application.

[0032] It is also desirable to use white plastic film for a base material. The film which prepared the layer which has white pigments (titanium oxide, barium sulfate, etc.) in the film [which made plastics contain white pigments, such as a small amount of barium sulfate, titanium oxide, and a zinc oxide, as a white film], rear-face, or ink absorption layer side can be used.

[0033] The stencil paper of the paper base material which covered both sides with polyolefine uses wood pulp as the main raw material, if needed, it adds synthetic fibers, such as synthetic pulps, such as polypropylene, or nylon, and polyester, and paper making is carried out. As wood pulp, although both LBKP, LBSP, NBKP, NBSP LDP and NDP LUKP and NUKP can be used, it is desirable to use more many [for a staple fiber] LBKP, NBSP (s), LBSP(s), and NDP(s) and LDP(s). However, it reaches LBSP or the ratio of LDP has 10 % of the weight or more and 70 desirable % of the weight or less.

[0034] Chemical pulp with few impurities (for example, sulfate pulp, sulfite pulp) is desirable, and pulp's is [the pulp which performed bleaching processing and raised the whiteness degree] useful.

[0035] Hara Kaminaka can add suitably flexible-ized agents, such as moisture hold-back agents, such as paper reinforcing agents, such as white pigments, such as sizing compounds, such as a higher fatty acid and an alkyl ketene dimer, a calcium carbonate, talc, and titanium oxide, starch, polyacrylamide, and polyvinyl alcohol, a fluorescent brightener, and polyethylene glycols, a dispersant, and quarternary ammonium salt, etc.

[0036] The freshness of BARUPU used for paper making has desirable 200-500 cc by convention of CSF, and 30 thru/or 70% have the desirable sum of weight % of the 24-mesh residue and weight % of the 42-mesh residue as which the fiber length after beating is specified to JIS-P -8207. In addition, as for weight % of the four-mesh residue, it is desirable that it is 20 or less % of the weight.

[0037] The basis weight of stencil paper has 60 thru/or desirable 250g, and 90 thru/or its 200g are especially desirable. The thickness of stencil paper has 50 thru/or desirable 250 micrometers.

[0038] After a paper-making phase or paper making, stencil paper can carry out calender processing and can also give the Takahira slippage. A stencil paper consistency has 0.7 thru/or common 1.2 g/m² (JIS-P -8118).

Furthermore, stencil paper stiffness has 20 thru/or desirable 200g on the conditions specified to JIS-P -8143.

[0039] A surface sizing compound may be applied to a stencil paper front face, and the sizing compound which can be added to said Hara Kaminaka as a surface sizing compound, and the same sizing compound can be used.

[0040] When measured by the hot water extraction method specified by JIS-P -8113, as for pH of stencil paper, it is desirable that it is 5-9.

[0041] although polyethylene is desirable and the polyethylene (LDPE) of a low consistency and the polyethylene (HDPE) of high density are used especially as polyolefine which covers a stencil paper front face and a rear face — other lines — low density polyethylene (LLDPE), polypropylene, etc. can be used.

[0042] As for the polyethylene layer by the side of an ink absorption layer, what added the titanium oxide of a rutile or an anatase mold, and improved opacity and a whiteness degree in polyethylene is desirable as widely performed by the printing paper for photographs. The content of titanium oxide is 5 - 15 % of the weight preferably three to 20% of the weight in general to polyethylene.

[0043] After preparing an ink absorption layer and a back layer, the amount of the polyethylene used of the front flesh side of stencil paper is chosen so that there may be no curl, damp and when it is saved by highly humidization. Usually, let thickness of the polyethylene layer by the side of 20-50 micrometers and a back layer be the range of 10-40 micrometers for the thickness of the polyethylene layer by the side of an ink absorption layer.

[0044] In this invention, the polyethylene covering paper base material which has the following properties can be used preferably.

A lengthwise direction by the reinforcement specified by :JIS-P -8113 in hauling strength ** 2 thru/or 30kg, a longitudinal direction — 20kg** tear: 1 thru/or on the strength — the convention approach by JIS-P -8116 — a lengthwise direction — 10 — or 300g a longitudinal direction — 20 thru/or 400g** Clerks stiffness: — 20-400cm³ / 100** compressibility: — two or more 103 Kgf/cm** surface smoothness: — the Beck smoothness specified to JIS-P -8119 500 seconds or more Especially, 1000 second or more ** surface roughness : about the wave filtration waviness curve drawn on with a cut-off value [of 0.8mm] conditions from the cross-section curve measured by the approach specified to JIS-B -0610 as 2.5mm of criteria length — wave filtration max — the time of measuring a wave — 100 point of measurement of the arbitration — max — a point 6 micrometers or more less than five pieces [a wave] The surface glossiness which the ten-point average of roughness height measured at the include angle of 75 degrees by the approach specified to less than 4 micrometer** surface glossiness:JIS-Z -8741 Moreover, 30% or more, When it measures by the approach especially indicated by 90% or more ** surface whiteness degree:JIS-Z -8722 preferably and displays 70% or more according to JIS-Z -8729 preferably, Especially 90% or more and (a'*₁, and b'*₁) L* 85% or more (-2 and 2), When it measures by the approach specified to (4, 2) and (4 -8) (-3, -8) being [it / in the color tone of the range surrounded] ** opacity:JIS-P -8138, 50% or more, 90% or more, it is the purposes, such as enlarging bond strength with a record

layer 94% or more especially most preferably at a base material, and it is desirable to perform corona discharge treatment, undercoating processing, etc. to a base material in advance of spreading of a record layer.

[0045] The ink jet record form of this invention has at least one-layer ink absorption layer on a base material. This ink absorption layer may be a swelling mold, or may be an opening mold, and may prepare both layer in the same on [a base material] side further.

[0046] A swelling layer is swollen at the same time it extends a liquid ink drop to a moderate size, when a liquid ink drop reaches the target, and it absorbs a liquid ink drop. The water in the ink absorbed by this swelling layer and other organic solvents evaporate gradually after that, and only the color which is finally a non-volatile component is substantially left behind into a coat.

[0047] The ink absorption layer of a swelling mold needs to show high bloating tendency to a liquid ink drop, and the hydrophilic binder in which liquid ink bloating tendency is shown is used as a main constituent. As a hydrophilic binder used preferably For example, gelatin or a gelatin derivative (phenylcarbamoyl-ized gelatin etc.), A polyvinyl pyrrolidone (about 200,000 or more have desirable average molecular weight), a pullulan, Polyvinyl alcohol or its derivative, a polyethylene glycol (100,000 or more have desirable average molecular weight), A carboxymethyl cellulose, hydroxyethyl cellulose, a dextran, A dextrin, polyacrylic acid and its salt, an agar, a kappa carrageenan, lambda-carrageenan, iota-carrageenan, xanthene gum, locust bean gum, A polyalkylene oxide system copolymerization nature polymer given in an alginic acid, gum arabic, JP,7-195826,A, and a 7-9757 official report, Polymers, such as independent or a copolymer which repeats and has these vinyl monomers of the vinyl monomer which has the carboxyl group and sulfonic group of a publication, can be mentioned to a water-soluble polyvinyl butyral or JP,62-245260,A. These hydrophilic binders may be used independently and may use two or more sorts together.

[0048] Since the ink absorption layer of a swelling mold needs to have the early permeability and the bloating tendency over liquid ink, it is desirable to contain at least one sort as which 200,000 or more polyvinyl pyrrolidones are chosen as for molecular weight, and about 50,000 or more polyethylene oxide and molecular weight are chosen for molecular weight from the copolymer of 100,000 or more polyethylene oxide and polypropylene oxide, hydroxyethyl cellulose, and polyacrylamide to the hydrophilic binder of the ink absorption layer of a swelling mold.

[0049] Considering the viewpoint of stabilization high-speed spreading, it is desirable to use reversibly a part of hydrophilic binder in which sol gel transformation is possible, and it is desirable to use at least one sort of gelatin, a gelatin derivative, and a kappa carrageenan from this point.

[0050] As for the binder used for the ink absorption layer of a swelling mold, what has gelatin or a gelatin derivative at least is desirable. The binder of the combination of the combination of gelatin or a gelatin derivative, the combination of a polyvinyl pyrrolidone and a gelatin derivative, polyvinyl alcohol, and its derivative, the combination of a gelatin derivative, a polyvinyl pyrrolidone, and polyvinyl alcohol, gelatin or gelatin, a polyalkylene glycol, and its derivative is used especially for the desirable ink absorption layer of a swelling mold as a binder.

[0051] As gelatin preferably used in the above, usual alkali treatment gelatin and acid-treatment gelatin are mentioned. The isoelectric point can choose the thing of the range of 9-5 suitably, and can use gelatin.

[0052] The gelatin which made the amino group or imino group of gelatin react with isocyanates, such as acid anhydrides, such as phthalic anhydride, and phenyl isocyanate, and made a part of amino group and imino group [at least] inactivate as derivative gelatin is used preferably.

[0053] When an ink absorption layer is a swelling mold, the range of 4-20 micrometers of desiccation thickness of an ink absorption layer is 6-15 micrometers preferably in general.

[0054] When an ink absorption layer is an opening mold, an opening is formed between solid particulates a hydrophilic property or a hydrophobic binder, inorganic, or organic.

[0055] Various methods can perform formation of an opening. The formation approach of the ink absorption layer of a typical opening mold is explained below.

[1] How to apply the uniform coating liquid containing two or more sorts of polymers which carry out phase separation on a base material, make carry out phase separation of these polymers in a desiccation process, and form an opening.

[2] How to apply the coating liquid containing a solid-state particle and a hydrophilic property, or a hydrophobic binder on a base material, to immerse in the liquid containing water or a suitable organic solvent in a record form after desiccation, make dissolve a solid-state particle, and create an opening.

[3] How to apply the coating liquid containing the compound which has the property which carries out heating foaming on a base material, make these compounds foam in a desiccation process, and form an opening into a coat.

[4] How to apply the coating liquid containing a porosity solid-state particle and a hydrophilic binder on a base material, and form an opening between the inside of a porosity particle, or a porosity particle.

[5] the solid-state particle which has the volume more than equivalence in general to a hydrophilic binder — and

— or the approach of applying the coating liquid which mixed the oil droplet particle on a base material, and drying and creating an opening between a hydrophilic binder, and a solid-state particle and an oil droplet particle.

[6] The approach mean particle diameter makes the solid-state particle in the coating liquid which made solid-state particle about 0.1 micrometers or less contain condense at the time of adjustment of coating liquid or coat formation, makes a secondary particle or the three-dimensional structure form, and creates an opening.

[0056] It is required it to be possible to add a cation mordant and to be able to adjust surface pH to 3-5 with any means of the above [the opening formation approach in the record form of this invention], although it is good. Moreover, the approach which is not complicated is desirable, considering the viewpoint which the glossiness on the front face of the recording paper is not much reduced, and creates it by low cost.

[0057] As an approach of making the desirable opening which hits carrying out this invention from the above viewpoint forming, the above [5] or the approach of [6] of desirable especially a desirable approach is the approach of [6].

[0058] In the ink absorption layer of an opening mold, a certain thing of the total amount (void volume) of an opening is [1m of record forms] desirable 20ml or more per two.

[0059] Although ink absorptivity is good when void volume is less than two 20 ml/m, and there are few amounts of ink at the time of printing, if the amount of ink increases, ink will not be absorbed completely, but image quality is reduced or it is easy to produce problems, like drying is late.

[0060] Although especially the upper limit of void volume is not restricted, in order for setting thickness of the ink absorption layer of an opening mold to 50 micrometers or less in general not to worsen the physical characteristic of coats, such as a crack, it is required, and it difficult to make void volume into two or less 40 ml/m, considering this point.

[0061] Setting to this invention, void volume is J.TAPPI Paper pulp test method No.51-87 It is expressed with the amount of liquid transition in absorption time amount 2 seconds (ml/m²) when it measures by the approach indicated by the liquid absorptivity test method (Bristow law) of paper and the paper board. In addition, in order to make distinction of measurement area easy, less than 2% of water soluble dye may be made to contain by the above-mentioned measuring method, although pure water (ion exchange water) is used for measurement.

[0062] In the ink absorption layer of an opening mold, the void volume to solid content capacity is called voidage. in this invention, making voidage into 200% or more especially 150% or more does not have a thick kink in thickness superfluously — since it comes out and an opening can be formed efficiently, it is desirable. Although the upper limit of voidage generally receives constraint from the reinforcement and film formation nature of a coat, it is usually less than 400%.

[0063] When making a solid-state particle contain and making the ink absorption layer of an opening mold form, as a solid-state particle, a well-known solid-state particle inorganic [various kinds of] or organic can be conventionally used in an ink jet record form.

[0064] As an example of the non-subtlety particle used for the above-mentioned purpose, white inorganic pigments, such as precipitated calcium carbonate, whiting, a magnesium carbonate, a kaolin, clay, talc, a calcium sulfate, a barium sulfate, a titanium dioxide, a zinc oxide, zinc hydroxide, zinc sulfide, zinc carbonate, a hydrotalcite, aluminum silicate, the diatom earth, a calcium silicate, a magnesium silicate, synthetic amorphous silica, colloidal silica, an alumina, a colloidal alumina, pseudo-boehmite, an aluminum hydroxide, a lithopone, a zeolite, and a magnesium hydroxide, etc. can be mentioned.

[0065] Homogeneity may distribute in the binder with the primary particle, and a non-subtlety particle forms secondary floc and may be distributed by homogeneity in the binder.

[0066] As an example of an organic particle, particles, such as polystyrene, polyacrylic ester, polymethacrylic acid ester, polyacrylamides, polyethylene, polypropylene, a polyvinyl chloride, polyvinylidene chlorides or these copolymers, a urea-resin, or melamine resin, are mentioned.

[0067] In this invention, a non-subtlety particle is desirable, considering the viewpoint that high voidage is obtained.

[0068] As for the above-mentioned inorganic particle, it is desirable that the particle size of a primary particle uses a thing 30nm or less. Especially the particle size of the primary particle of a desirable non-subtlety particle is 20nm or less.

[0069] When the mean diameter of a primary particle uses the particle exceeding 30nm, floc which the cation mordant of a water-soluble polymer mold and condensation become easy to take place, and formed will also be made big and rough, and glossiness will fall.

[0070] Especially although especially the minimum of the particle size of a primary particle is not limited, 3nm or more is 6nm or more in general from the viewpoint on manufacture of a particle.

[0071] The mean particle diameter of a non-subtlety particle observes the particle which appeared in the cross section and front face of an ink absorption layer of the particle itself or an opening mold with an electron microscope, and is called for as the arithmetic average value (individual number average) in quest of the particle

size of the particle of 100 arbitration. The particle size of the particle of each [here] is expressed with the diameter when assuming a circle equal to the projected area.

[0072] As a non-subtlety particle, it is desirable that it makes the ratio of the non-subtlety particle which exceeds 30nm in this case 50 or less % of the weight to all inorganic particles although the mean particle diameter of a primary particle is possible also for the non-subtlety particle and mean particle diameter of 30nm or less using together a non-subtlety particle 30nm or more, and 20 or less % of the weight is more desirable.

[0073] Considering the point of that a clear image is recordable, being able to manufacture by low cost that an image with high concentration is formed, as a solid-state particle, it is desirable to use the solid-state particle chosen from the particle silica, the colloidal silica and the alumina, or hydrated alumina compounded by the gaseous-phase method.

[0074] The alumina or hydrated alumina preferably used in this invention is the porosity alumina whose radius is 3-10nm and whose sum of pore volume is 0.2 - 2 ml/g, or its hydrated compound. Pore volume can be measured with a well-known nitrogen adsorption process.

[0075] An alumina or hydrated alumina may be crystallinity, may be amorphous, and can use the thing of the configuration of arbitration, such as an indeterminate form particle, a spherical particle, and a needlelike particle.

[0076] The particle silica compounded by the gaseous-phase method can burn and obtain a silicon tetrachloride at an elevated temperature with hydrogen and oxygen, and is usually silica powder whose particle diameter of a primary particle is 5-500nm. What has the primary particle diameter of 30nm or less especially is desirable in respect of glossiness.

[0077] The particle silica compounded by current and such gaseous-phase method is marketed, and there is various kinds of Aerosil of Japanese Aerosil in a commercial particle silica.

[0078] The colloidal silica preferably used by this invention carries out double decomposition of the specific silicate with an acid etc., or carries out heating aging of the silica gel which is made to pass an ion-exchange-resin layer and is obtained, and is obtained. Using this colloidal silica for an ink jet record form For example, JP,57-14091,A, a 60-219083 official report, A 60-219084 official report, a 61-20792 official report, a 61-188183 official report, A 63-17807 official report, this JP,4-93284,A, a 5-278324 official report, A 6-92011 official report, a 6-183134 official report, a 6-297830 official report, It is indicated by a 7-81214 official report, the 7-101142 official report, the 7-179029 official report, the 7-137431 official report, the international patent public presentation WO 94/No. 26530 official report, etc.

[0079] Although the particle diameter of colloidal silica is 5-100nm, its thing with a particle diameter of 7-30nm is usually desirable.

[0080] The particle silica and colloidal silica which were compounded by the gaseous-phase method may carry out cation conversion of the front face, for example, may process a front face by mineral salt, such as aluminum, calcium, Mg, and Ba.

[0081] Also in the above-mentioned opening morphogenetic substance, a particle silica is desirable especially in this invention, it is most suitable for performing opening formation of the above [6] especially, and a particle is the silica compounded by the gaseous-phase method.

[0082] A hydrophilic binder is used in order to give the property as a coat to the ink absorption layer of the above-mentioned opening mold.

[0083] Although various kinds of well-known binders used for the ink absorption layer of a swelling mold as these binders can be used conventionally, the binder which swells in the early phase where the liquid ink drop which reached the target permeated, and does not take up an opening substantially is desirable. Especially a desirable hydrophilic binder is polyvinyl alcohol of completeness or partial saponification from this point. In addition, cation denaturation polyvinyl alcohol, anion denaturation polyvinyl alcohol, and Nonion denaturation polyvinyl alcohol are also contained in polyvinyl alcohol here.

[0084] Especially as for desirable polyvinyl alcohol, whenever [saponification] are 80 or more partial saponification polyvinyl alcohol or full saponification polyvinyl alcohol.

[0085] a comparatively high-polymer thing [considering the viewpoint in which the polymerization degree of polyvinyl alcohol improves coat brittleness] — good — average degree of polymerization — 1000-5000 — the thing of 2000-4000 is used especially preferably.

[0086] Cation conversion polyvinyl alcohol is polyvinyl alcohol which has the 1-3rd class amino group which is indicated by JP,61-10483,A, and the 4th class ammonium in the principal chain of polyvinyl alcohol, or a side chain, and it is obtained by saponifying the copolymer of the ethylenic unsaturated monomer and vinyl acetate which have a cationic radical.

[0087] As an ethylenic unsaturated monomer which has a cationic radical For example, TORIMECHIRU-(2-acrylamide -2, 2-dimethyl ethyl) ammoniumchloride, TORIMECHIRU-(3-acrylamide -3, 3-dimethyl propyl) ammoniumchloride, N-vinyl imidazole, N-vinyl-2-methylimidazole, N-(3-dimethylaminopropyl) methacrylamide, Hydroxyl ethyl trimethylammonium chloride, TORIMECHIRU-(methacrylamide propyl) ammoniumchloride, N-(1 and 1-dimethyl-3-dimethylaminopropyl) acrylamide, etc. are mentioned.

[0088] the copolymer of the ethylenic unsaturated monomer and vinyl acetate which have a cationic radical — setting — the ratio of a cation denaturation radical content monomer — vinyl acetate — receiving — 0.1-10-mol % — it is 0.2-5-mol % preferably.

[0089] Although the thing of polymerization degree 500-4000 is used, as for cation denaturation polyvinyl alcohol, 1000-4000 are usually desirable.

[0090] The copolymer of vinyl alcohol which is indicated by the polyvinyl alcohol and JP,61-237681,A which have an anionic radical which is indicated by JP,1-206088,A as anion denaturation polyvinyl alcohol, for example, and the 63-307979 official report, and the vinyl compound which has a water-soluble radical, and the denaturation polyvinyl alcohol which has a water-soluble radical which is indicated by JP,7-285265,A are mentioned.

[0091] The polyvinyl alcohol derivative which added a polyalkylene oxide radical which is indicated by JP,7-9758,A to a part of vinyl alcohol as Nonion denaturation polyvinyl alcohol, for example, and the block copolymer of the vinyl compound and vinyl alcohol which have the hydrophobic radical indicated by JP,8-25795,A are mentioned.

[0092] Although polyvinyl alcohol is mainly used, other hydrophilic binders can also be made to contain as a binder of the ink absorption layer of an opening mold. As for other hydrophilic binders, it is desirable that it is 20 or less % of the weight in general to polyvinyl alcohol.

[0093] When an ink absorption layer is an ink absorption layer of an opening mold, in the case of the approach [5] of differing by the formation approach of an opening and making said opening forming, the weight ratios to the hydrophilic binder of a solid-state particle are 6-100 in general, and, in the case of the approach [6] of making an opening forming, are 2-10.

[0094] In the ink jet record form of this invention, a cation mordant is contained with a hydrophilic binder in an ink absorption layer.

[0095] Although the polymer mordant which has the class [1st] - 3rd class amino group and a quarternary-ammonium-salt radical can be used as a cation mordant, since there being little discoloration by the passage of time and light-fast degradation and the mordanting ability of a color are high enough, the polymer mordant which has a quarternary-ammonium-salt radical is desirable.

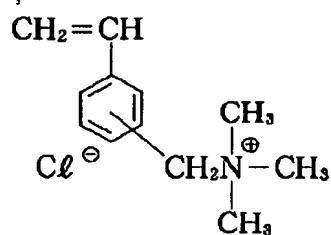
[0096] A desirable polymer mordant is the homopolymer of the monomer which has a quarternary-ammonium-salt radical, a copolymer with other monomers, or a condensation polymerization object.

[0097] The example of the monomer which has the quarternary-ammonium-salt radical preferably used for below is expressed.

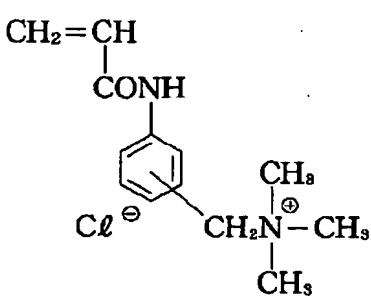
[0098]

[Formula 1]

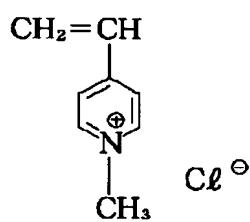
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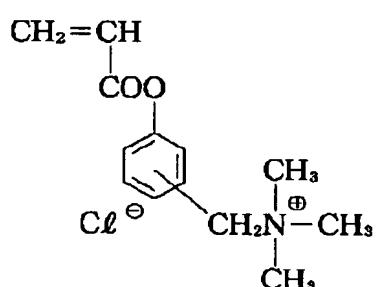
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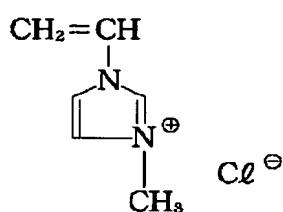
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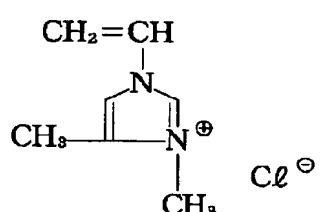
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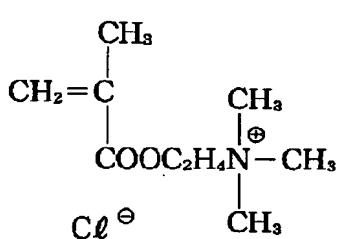
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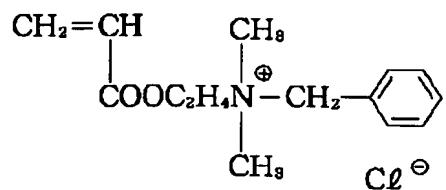
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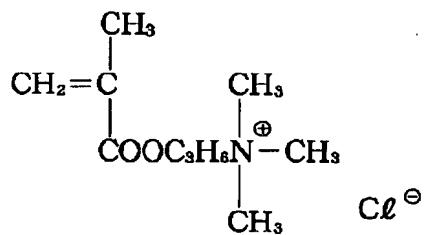
[0099]

[Formula 2]

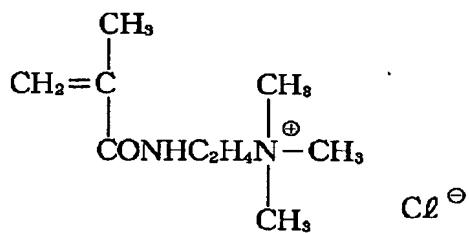
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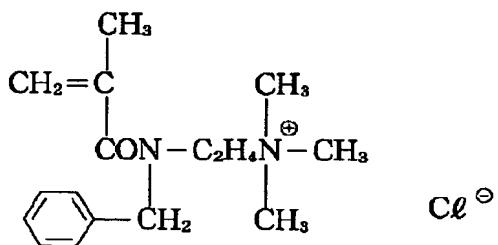
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10



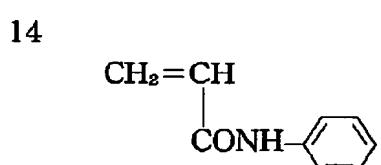
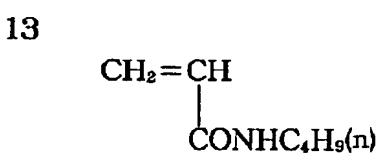
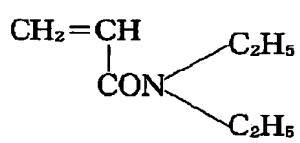
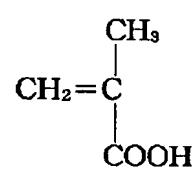
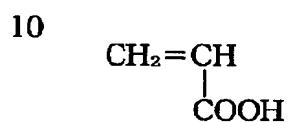
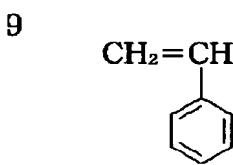
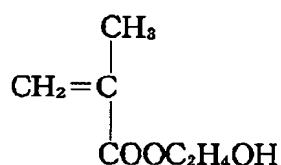
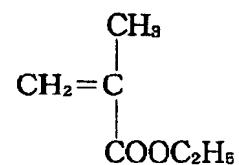
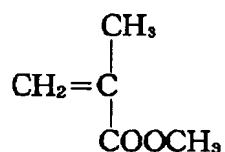
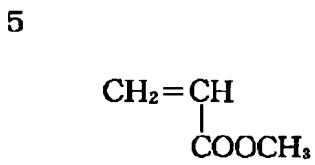
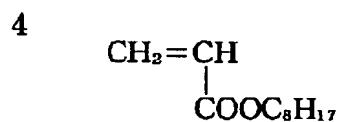
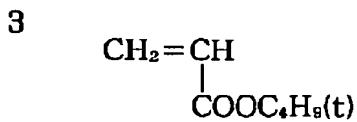
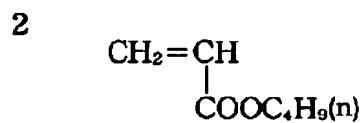
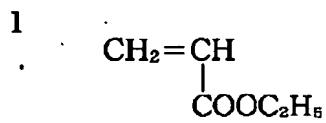
11



上記モノマーと共に重合し得るモノマーの具体例を次に示す。

[0100]

[Formula 3]

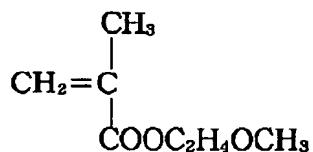


[0101]
[Formula 4]

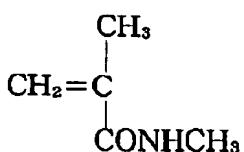
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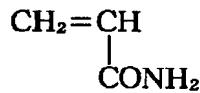
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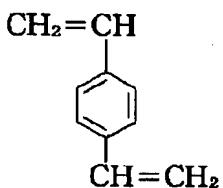
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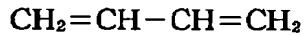
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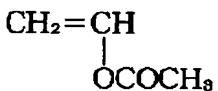
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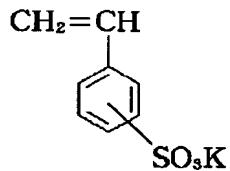
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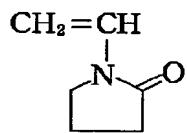
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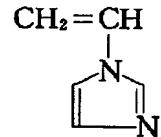
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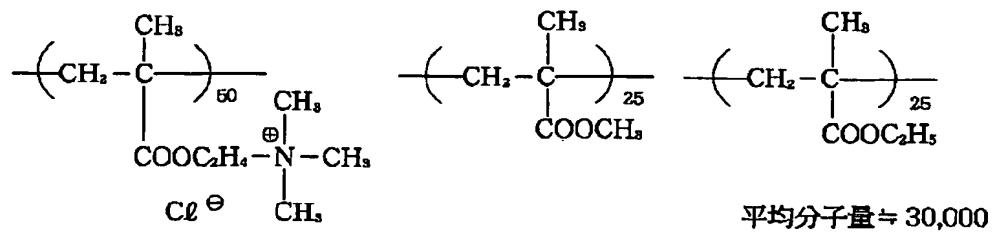


The example of a polymer mordant of having the quarternary-ammonium-salt radical preferably used for below is shown. (A numeric value expresses mol %.)

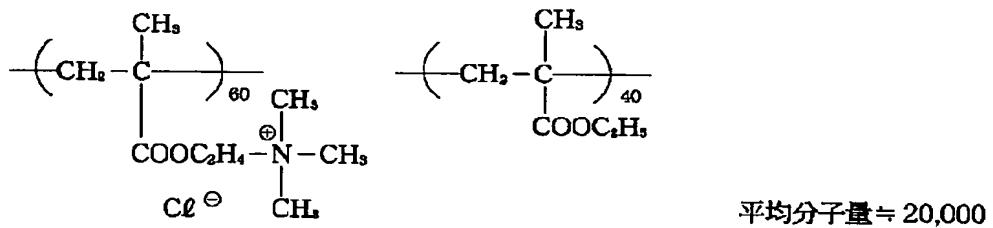
[0102]

[Formula 5]

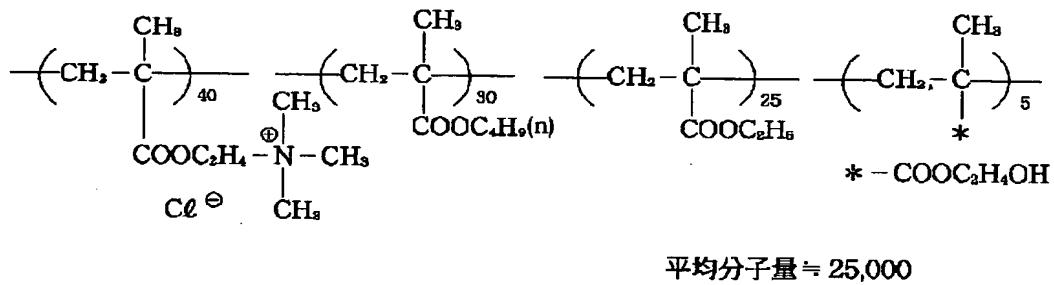
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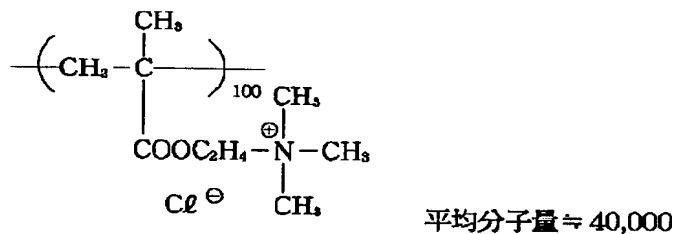
Mor - 2



Mor - 3



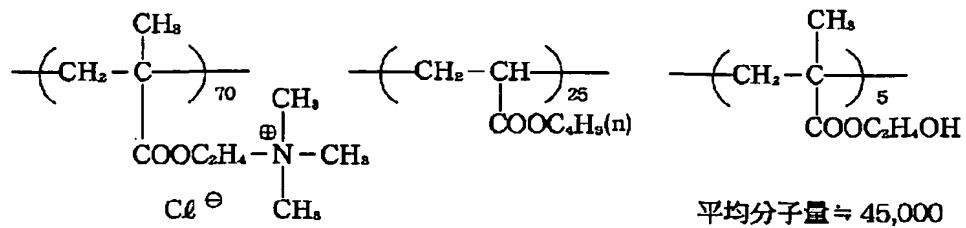
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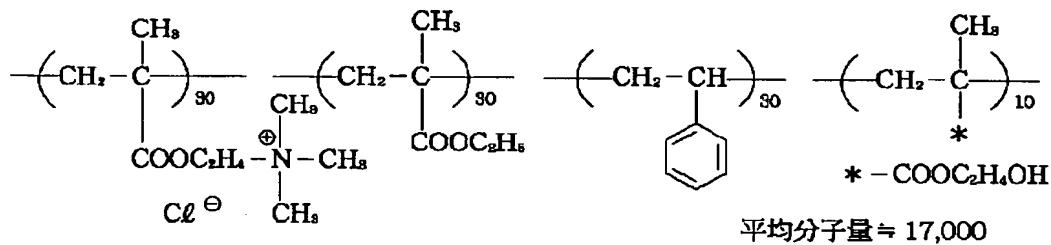
[0103]

[Formula 6]

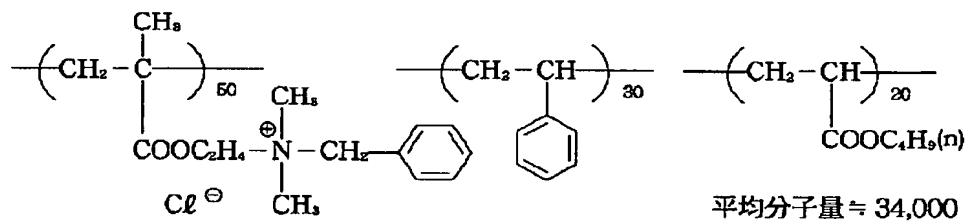
Mor - 5



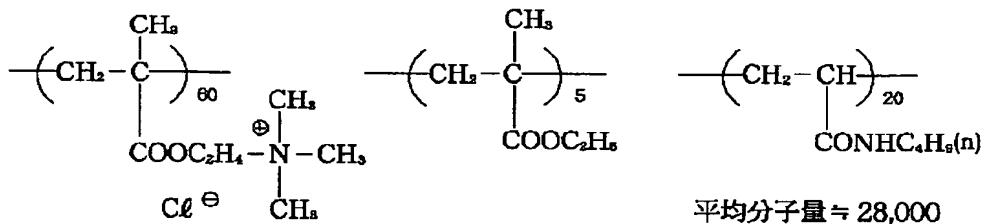
Mor - 6



Mor - 7



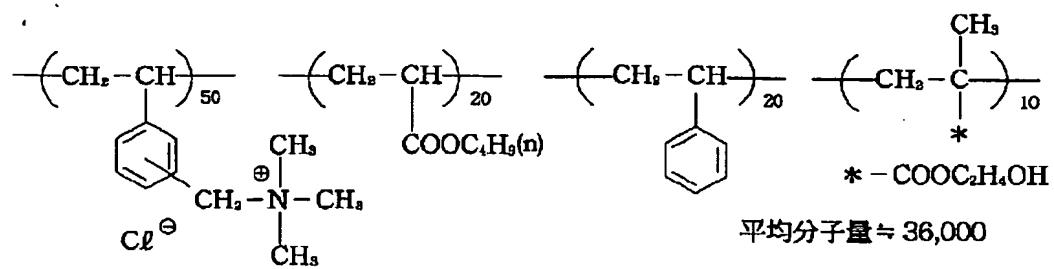
Mor - 8



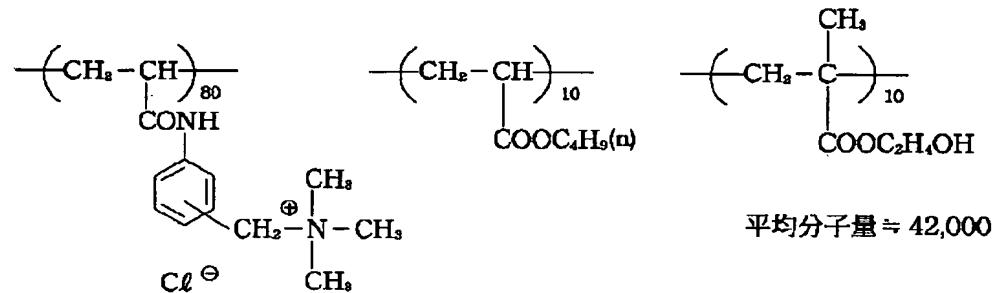
[0104]

[Formula 7]

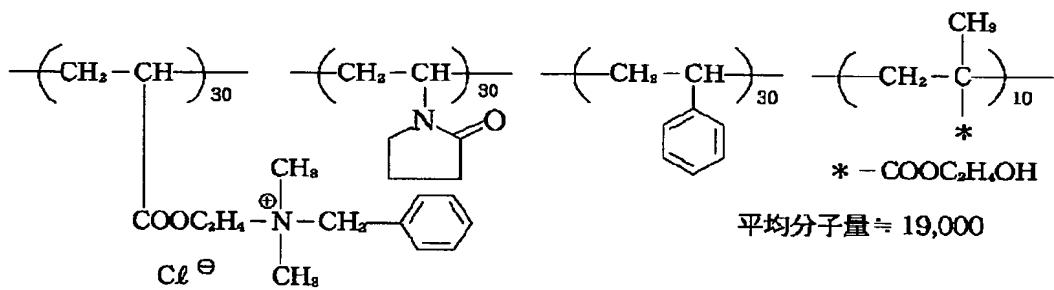
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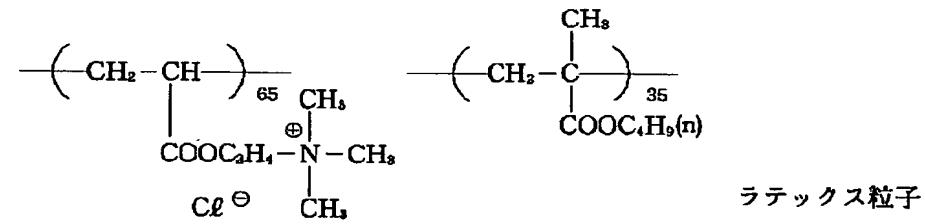
Mor - 10



Mor - 11



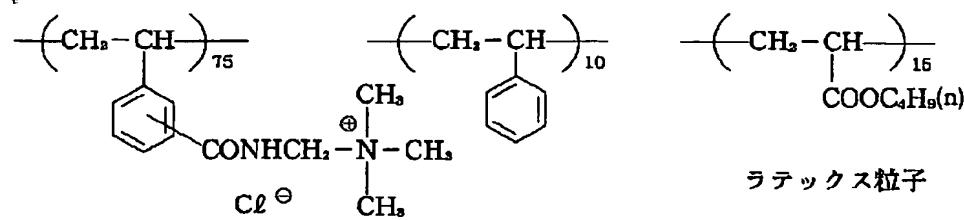
Mor - 12



[0105]

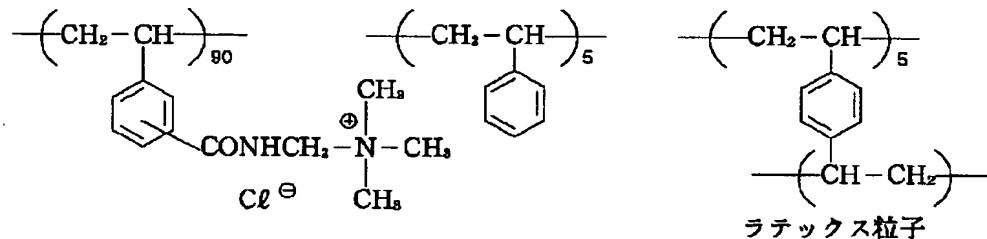
[Formula 8]

Mor-13



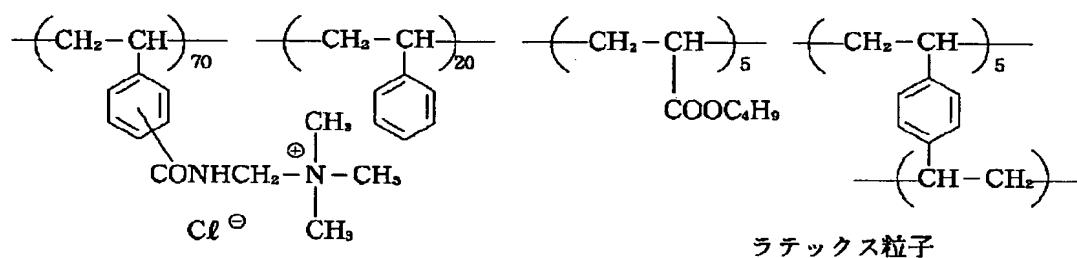
ラテックス粒子

Mor-14



ラテックス粒子

Mor-15



ラテックス粒子

Even if a cation mordant is a polymer mordant which consists of a water-soluble polymer, it may be a polymer mordant which consists of a latex particle compounded by the emulsion polymerization. When an ink absorption layer is an ink absorption layer of a swelling mold and a latex mordant is [an ink absorption layer] an ink absorption layer of an opening mold again, a water-soluble polymer mordant is desirable.

[0106] Since a cation site contributes to a water resisting property or damp-proof amelioration effectively since condensation with a non-subtlety particle has few cation mordants whose mean molecular weights are 50,000 or less, and glossiness cannot deteriorate easily in a water-soluble cation mordant, it is desirable.

[0107] Desirable average molecular weight is 30,000 or less. The minimum of average molecular weight is 2000 or more more nearly about than a water resisting property or a damp-proof viewpoint, although there is especially no constraint.

[0108] A mean molecular weight says the polystyrene reduced property which is the thing of number average molecular weight and was calculated from the gel bar MIESHON chromatography here.

[0109] Although an ink absorption layer changes with concentration, recording density, etc. of a color of recording ink further in absorptivity or non-absorptivity, generally as for the amount of the mordant used, a swelling mold, an opening mold, and 0.2-10g per two of base materials are preferably used for it in 0.5-5g 1m of record forms.

[0110] A record form is an opening mold, when the water-soluble polymer is used as a cation mordant, the ratio of a cation mordant and a non-subtlety particle is important, and it is desirable that the ratios of the cation mordant to a non-subtlety particle are 0.01-0.3 in a weight ratio.

[0111] Curl tends to become a problem, when a water resisting property and damp-proof effectiveness tend to become inadequate and 0.3 is exceeded in the case of less than 0.01.

[0112] In this invention, it is required to make the film surface pH by the side of the recording surface of an ink jet record form into a specific value (3 or more [i.e.,]) and 5 or less range.

[0113] In the record form of this invention, since the film surface pH by the side of the recording surface of an ink jet record form was selected to the specific value, a best water resisting property and best moisture resistance can be acquired by use of the cation mordant of the need minimal dose, the amount of the cation mordant used can be pressed down to the minimum, and it can prevent the defect by abundant use of a cation mordant arising.

[0114] In case ink jet record is carried out although a water resisting property and moisture resistance improve sharply when a film surface pH is less than three, the moment recording ink contacted the record form front face, a color condenses, or a color deposits on a front face by the passage of time after record, the good maximum concentration is not obtained or a poor color tone is caused.

[0115] When a film surface pH exceeds 5, a water resisting property and moisture resistance become inadequate, and a damp-proof fall is especially large.

[0116] When the film surface pH exceeded 5 and it is saved under highly humid after printing, the mobility of a color increased with the moisture incorporated in the ink absorption layer, and although the reason a film surface pH affects moisture resistance is not certain, even if the thione mordant contains, I think that a color will spread.

[0117] The blot after this printing tends to take place by the time of the high-boiling point organic solvent of hydrophilic properties, such as a glycerol and a diethylene glycol, which it is more remarkable to save under highly humid from immediately after printing, and is contained in recording ink having not evaporated from a coat.

[0118] When saved under highly humid, in order for each dot printed with the ink jet printer to pass and to spread in the time, it appears as concentration change especially in the highlights section or a middle concentration region.

[0119] Since it is thought that a film surface pH will change when it dips underwater, the reason a film surface pH affects a water resisting property is not certain, but when a film surface is specific pH, even if a color dyes to a mordant firmly and is dipped underwater, the thing which outflow-comes to be hard is presumed.

[0120] Setting to this invention, a film surface pH is a J.TAPPI paper pulp test method. According to the approach of a publication, the front face pH measured after 30 seconds is said to No.49 using distilled water.

[0121] It is the approach of setting pH of the coating liquid which forms ** ink absorption layer as the value which was able to be decided beforehand as an approach of adjusting a film surface pH to the range of this invention (3 or more [i.e.,]), and 5 or less, and setting to the target pH after spreading desiccation.

** How to carry out the OBAO coat of the liquid of suitable pH, to dry and to acquire the target pH after spreading desiccation of an ink absorption layer.

** How to dip and dry in the water solution of suitable pH after spreading desiccation of an ink absorption layer. **** is mentioned.

[0122] Considering the point that the manufacture approach is simple among the approaches of the above-mentioned ** - **, the approach of ** is desirable.

[0123] ** When enforcing an approach, pH of coating liquid and pH of the film surface of a dry paint film are required in order that asking for pH of coating liquid and relation with a film surface pH by experiment etc. beforehand since it is not necessarily in agreement may make it the target film surface pH.

[0124] Accommodation of a film surface pH is performed combining various kinds of acids or alkali suitably.

[0125] As an acid, organic acids, such as inorganic acids, such as a hydrochloric acid, a nitric acid, a sulfuric acid, and phosphoric acid, an acetic acid, a citric acid, and a succinic acid, are used, and hydroxylation NATORIMU, a potassium hydroxide, a calcium hydroxide, aqueous ammonia, potassium carbonate, a sodium carbonate, trisodium phosphate, triethanolamine, etc. are used as alkali, for example.

[0126] Otherwise in an ink absorption layer, various additives can be added. Hereafter, it explains.

[0127] In the ink absorption layer of the record form of this invention, the hardening agent which can construct a bridge in a hydrophilic binder can be added.

[0128] When an ink absorption layer is an ink absorption layer of a swelling mold, since the rate of absorption of ink falls notably by dura-mater-izing, the amount of the hardening agent used should be made the minimum.

[0129] Since ink rate of absorption is improved by dura-mater-izing when an ink absorption layer is an ink absorption layer of an opening mold, it is desirable to construct a bridge in a hydrophilic binder. Ink rate of absorption is improved by carrying out the dura mater of the hydrophilic binder, because the bloating tendency over the liquid ink of a hydrophilic binder is controlled and lock out of an opening is prevented.

[0130] A hardening agent is a compound which has the various functional groups which the hydrophilic binder has, and the radical which can react, for example, is a compound which has an epoxy group, a formyl group, an ethylene imino group, an activity vinyl group, etc.

[0131] Although the addition of a hardening agent changes greatly with differences in an ink absorption layer like the above, in a swelling mold, it is 5-500mg per hydrophilic binder 1g in 0.1-20mg per hydrophilic binder 1g, and an opening mold.

[0132] In polyvinyl alcohol desirable as a hydrophilic binder used by this invention, it is desirable to add a way acid and/or way sand as a hardening agent. The amount of a way acid and/or the way sand used is 50-500mg per polyvinyl alcohol 1g.

[0133] In addition to the above, for example, an ultraviolet ray absorbent given in JP,57-74193,A, a 57-87988 official report, and a 62-261476 official report, JP,57-74192,A, a 57-87989 official report, a 60-72785 official

report, The fading inhibitor indicated by a 61-146591 official report, JP,1-95091,A, the 3-13376 official report, etc., An anion, a cation or the various surfactants of non-ion, JP,59-42993,A, The fluorescent brightener indicated by a 59-52689 official report, a 62-280069 official report, a 61-242871 official report, JP,4-219266,A, etc., Various well-known additives, such as lubricant, such as a defoaming agent and a diethylene glycol, antiseptics, a thickener, an antistatic agent, and a mat agent, can also be made to contain.

[0134] The ink jet record form of this invention may have the ink absorption layer more than two-layer in the same base material side. In this case, an ink absorption layer may be an ink absorption layer of a swelling mold, or may be an ink absorption layer of an opening mold.

[0135] The following are mentioned as an example of concrete lamination.

** The record form which consists only of the ink absorption layer of an opening mold (the multistory configuration of the ink absorption layer of an opening mold is included.).

** The record form which consists only of the ink absorption layer of a swelling mold (the multistory configuration of the ink absorption layer of a swelling mold is included.).

** The record form which the ink absorption layer of a swelling mold is prepared in a lower layer, and has the ink absorption layer of an opening mold in the upper layer (the case where each layer has become more than two-layer is included.).

** The record form which the ink absorption layer of an opening mold is prepared in a lower layer, and has the ink absorption layer of a swelling mold in the upper layer (the case where each layer has become more than two-layer is included.).

[0136] In the ink jet record form of this invention, in order to adhere at the time of laying on top of the opposite side immediately after curl prevention and printing and to aim at prevention of a ** ink imprint, as for an ink absorption layer, it is desirable to prepare the back layer of various classes.

[0137] Although a back layer changes also with the class of base material, thickness, and the configuration and thickness of an ink absorption layer, generally a hydrophilic binder and a hydrophobic binder are used as a binder. The range of the thickness of a back layer is usually 0.1-10 micrometers.

[0138] Moreover, it can adhere to a back layer as other record forms, and a front face can be split-face-ized to prevention, amelioration of note nature, and a pan for amelioration of the conveyance nature within an ink jet recording device. The organic or inorganic particle whose particle size is 2-20 micrometers can be used for split-face-ization.

[0139] Next, when carrying out ink jet record using the record form of this invention, the aquosity recording ink to be used is explained.

[0140] Aquosity recording ink usually consists of an additive of water soluble dye and a solvent object, and others. Although water soluble dye, such as direct dye used by well-known ink jet record as water soluble dye, acid dye, basic dye, reactive dye, or a food dye, can be used, direct dye or acid dye is desirable.

[0141] Although the solvent of aquosity recording ink makes water a subject, when recording ink dries, a color deposits, and in order to prevent starting blinding in a nozzle tip or an ink supply path, a high-boiling point organic solvent with the boiling point liquefied above about 120 degrees C is usually added at a room temperature. It is required that it should have vapor pressure with far lower required therefore than water having the operation which prevents that formed elements, such as a color, deposit when water evaporates, and a big and rough sludge generates a high-boiling point organic solvent. Moreover, the miscibility over water needs to be high.

[0142] As a high-boiling point organic solvent used for such the purpose For example, ethylene glycol, propylene glycol, a diethylene glycol, Triethylene glycol, a glycerol, the diethylene-glycol monomethyl ether, The diethylene-glycol monobutyl ether, the triethylene glycol monobutyl ether, The glycerol monomethyl ether, 1 and 2, 3-butane triol, 1 and 2, 4-butane triol, 1, 2, 4-** NTAN triol, 1 and 2, 6-hexane triol, thiodiglycol, triethanolamine, a polyethylene glycol (average molecular weight is about 300 or less), etc. are mentioned. Moreover, dimethylformamide, N-methyl pyrrolidone, etc. can be used also besides having described above.

[0143] Also in the high-boiling point organic solvent of these many, the low-grade alkyl ether of polyhydric alcohol, such as polyhydric alcohol, such as a diethylene glycol, triethanolamine, a glycerol, and triethanolamine, and the triethylene glycol monobutyl ether, etc. is desirable.

[0144] As an additive of others which water color ink contains, a pH regulator, a sequestering agent, an antifungal agent, a viscosity controlling agent, a surface tension regulator, a wetting agent, a surfactant, a rust-proofer, etc. are mentioned, for example.

[0145] Water color ink is the purpose which wettability to a record form is made [purpose] good, or stabilizes the regurgitation from an ink jet nozzle, and it is desirable in 25 degrees C to have the surface tension of 28 - 40 dyne/cm within the limits preferably 25 to 50 dyne/cm.

[0146] Moreover, in 25 degrees C, 2 - 10cp is desirable still more desirable, and the viscosity of water color ink is usually 2.5 - 8cp.

[0147] In the ink jet record approach of this invention, it is desirable in the effectiveness of this invention to

make pH of recording ink into 3 or more and 8 or less to that of the maximum *****.

[0148] By making pH of recording ink or less into eight, it is recorded in the environment where relative humidity exceeds 80% especially when it combines with the ink jet record form of this invention, and when saved in the condition as it is, the amelioration effectiveness over moisture resistance becomes large.

[0149] If pH of recording ink becomes less than three, the stability of water soluble dye falls, and it will become or will become easy to corrode for blinding a lifting and the quality of the material of the various kinds in the ink liquid supply path in an ink jet printer which becomes empty.

[0150] Furthermore, pH of desirable recording ink is 3.5-7.

[0151] When the capacity of the liquid ink drop breathed out from an ink nozzle is 1-30pL, since the diameter of a dot with a diameter of about 20-60 micrometers is obtained in the record paper, it is desirable. The color-print printed with such a diameter of a dot gives a high-definition image. Furthermore, the capacity of a desirable liquid ink drop is 2-20pL.

[0152] Moreover, at least, when carrying out ink jet record by the recording method using the aquosity recording ink which is two kinds from which concentration differs more than twice in a Magenta and cyanogen, since low-concentration ink is used, it is hard coming to carry out discernment of a dot in the highlights section, but also when this recording method is used, these faults do not produce this invention.

[0153] In the ink jet record approach, various kinds of well-known methods can be conventionally used as the record approach. The detail of the record approach is indicated by the trend (the volume for Koichi Nakamura, March 31, Heisei 7, the Japan science-information incorporated company issue) of for example, an ink jet record technique.

[Translation done.]

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
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EXAMPLE

[Example] This invention is not limited by these examples although an example explains this invention concretely below.

[0155] The paper base material which covered both sides of the stencil paper for photographs of example 1160 g/m² with polyethylene (the polyethylene layer which contains an anatase mold titanium dioxide with a thickness of 35 micrometers 13% of the weight is formed in the recording surface side.) As for thickness, a polyethylene layer is formed in a rear-face side by 25 micrometers, and the back layer which makes a mat agent the silica 0.6 g/m² and whose mean diameter are about 13 micrometers, and contains it two times 0.3 g/m is formed on it by making Tg=65 degree C acrylic latex resin into solid content. It prepared.

<Production of coating liquid 1-1> In 900ml of pure water, it added, while the mean diameter of a primary particle agitated 180g of particle silica powder compounded by the gaseous-phase method which is about 7nm with the high-speed homogenizer, and the silica water dispersion was produced. Next, in this silica water dispersion, 100ml of 25% water solutions of instantiation mordant Mor-1 (cation mordant) was added, the high-speed homogenizer distributed for 30 minutes, and pale clear dispersion liquid were obtained. Next, average degree of polymerization added 1ml of 10% polyvinyl alcohol water solutions whenever [saponification / whose] is 88% by 300, and average degree of polymerization added gradually further 530ml (ethyl acetate is contained 4% of the weight) of 5% polyvinyl alcohol water solutions whenever [saponification / whose] is 88% by 3500. Subsequently, 40ml of borated water solutions was added 4% as a hardening agent, and 20ml ethanol was added, and the coating liquid 1-1 which adds 50ml of gelatin water solutions 10%, and forms the ink absorption layer of an opening mold further was produced.

<Production of the record form 1-1> The coating liquid 1-1 warmed at 40 degrees C was applied so that humid thickness might be set to 260 micrometers at the recording surface side of the paper base material which covered above-mentioned both sides with polyethylene, and it cooled so that spreading coat temperature might become 15 degrees C or less (for 20 seconds). Subsequently, the 40-degree C wind was sprayed for the 30-degree C wind for 60 seconds for 60 seconds, for 120 seconds and a 35 more-degree C wind were sprayed for 60 seconds and for a 50-degree C wind one by one for 60 seconds, the 25-degree C wind was dried, further, 25 degrees C and the ambient atmosphere of 50% of relative humidity were passed for 120 seconds, gas conditioning was carried out, and the record form 1-1 was produced.

[0156] The film surface pH of the obtained record form 1-1 is shown in Table 1.

<Production of the record form 1-2 to 1-5> pH of coating liquid 1-1 was changed using the nitric acid or the sodium hydroxide, and the record form 1-2 to 1-5 as well as the record form 1-1 was produced.

[0157] The film surface pH of the obtained record form 1-2 to 1-5 is shown in Table 1.

[0158] About the obtained record form 1-1 to 1-5, void volume, ink absorptivity, glossiness, curl, a water resisting property, moisture resistance, lightfastness, and maximum density were evaluated by the following.
1 Void volume Kumagaya Riki Kogyo K.K. make and a Bristow testing-machine II mold (pressure type) were used, and the amount of transition for [contact time] 2 seconds (ml/m²) was calculated as void volume.

2 Ink absorptivity Kumagaya Riki Kogyo K.K. make and a Bristow testing-machine II mold (pressure type) were used, and contact time calculated ink absorptivity from the amount of transition in 0.5 seconds (ml/m²).

3 The specular gloss was measured 75 degrees with the deflection photometer (VGS-101DP) by glossiness Nippon Denshoku Industries Co., Ltd.

4 The sample of A5 size was left for 30 minutes by the environment where curl 23degree C and relative humidity are 20%, and the environment where 30 degrees C and relative humidity are 80%, and the height of four corners was measured by them, they were asked for the average, and curl was evaluated by them. When a recording surface was turned up, a record form was laid on a base, the edge of a record form was higher than the base top, + and a recording surface were turned down, a record form was laid on a base, and the edge of a record form was higher than the base top, the height of curl was displayed as -. If there is this height by **10mm or less, it will be satisfactory in general practically.

[0159] **5** The on-demand mold ink jet printer was used for the waterproof record form, and it printed so that reflection density might be set to about 1.0 with the recording ink of the Magenta ink of the following

presentation. After printing, after being immersed into pure water at the room temperature for 12 hours, reflection density was measured again.

[0160] The survival rate of the reflection density after immersion was searched for from the reflection density before being immersed in pure water, and it considered as the water resisting property.
(Presentation of the recording ink of Magenta ink)

Pure water 75ml Diethylene glycol 10.3g Glycerol 7.3g C9H19O(CH₂OCH₂O)10H 0.05g DirectRed227 After 1.7g sodium hydroxide / sulfuric acid adjusts to pH=5.0**0.1, 100ml is made with pure water.

6 The on-demand mold ink jet printer was used for the damp-proof record form under 23 degrees C and the environment of 80% of relative humidity, and it printed so that reflection density might be set to about 0.5 with the recording ink of the Magenta ink of the above-mentioned presentation. It was left in the state of [as it is] after printing for 48 hours. The rate of change (with no concentration change of 0%) of the reflection density after the neglect to the reflection density immediately after printing was investigated, and it considered as moisture resistance.

7 The on-demand mold ink jet printer was used for the light-fast record form, and it printed so that reflection density might be set to about 1.0 with the recording ink of the Magenta ink of the above-mentioned presentation. The reflection density after 100-hour Mitsuteru putting and an optical exposure was measured in the printed record form using xenon fade meter, and it asked for the ratio of the reflection density after the optical exposure to the reflection density before an optical exposure as a coloring matter survival rate, and considered as lightfastness.

8 The on-demand mold ink jet printer was used for the maximum-density record form, it printed on the conditions from which the maximum density of a Magenta is obtained with the recording ink of the Magenta ink of the following presentation, the reflection density was measured, and it considered as maximum density.

[0161] The above result was shown in Table 1.

[0162]

[Table 1]

記録用紙	膜面pH	空隙容量	インク吸収性	光沢度	カール (mm)		耐水性 (%)	耐湿性 (%)	耐光性 (%)	最大濃度	
					23°C/20%	30°C/80%					
1-1	比較例	5.5	38.0	24.0	62.0	+3.0	-3.0	83.4	+25	72	2.09
1-2	本発明	4.5	37.5	24.5	62.7	+3.0	-2.5	89.6	+7	70	2.04
1-3	本発明	4.0	37.5	23.5	63.3	+3.5	-3.0	90.4	+4	70	2.05
1-4	本発明	3.5	37.0	23.0	61.8	+2.5	-2.0	92.2	+2	69	2.00
1-5	比較例	2.5	37.5	23.5	63.6	+2.5	-3.0	95.3	+2	63	1.73

[0163] The result of Table 1 shows improving both moisture resistance and a water resisting property, without the record form 1-2 to 1-4 which adjusted the film surface pH to the range of 3-5 almost having a bad influence on void volume, ink absorptivity, glossiness, curl, and lightfastness.

[0164] On the other hand, the record form 1-1 whose film surface pH is 5.5 is inferior, although a water resisting property is low a little and especially moisture resistance contains the cation mordant. Moreover, the remarkable fall of the maximum concentration expected to follow a water resisting property and moisture resistance on crystallization of a color although the record form 1-5 which set the film surface pH to 2.5 is excellent is accepted.

[0165] The record form 2-1 to 2-5 which has the film surface pH which shows example-2 instantiation mordant Mor-1 for an instantiation mordant in Table 2 like an example -1 except having changed into Mor-4 was produced. About the obtained record form 2-1 to 2-5, void volume, ink absorptivity, glossiness, curl, a water resisting property, moisture resistance, lightfastness, and maximum density were evaluated like the example -1. The obtained result is shown in Table 2.

[0166]

[Table 2]

記録用紙		表面pH	空隙容量	インク吸収性	光沢度	カール (mm)		耐水性 (%)	耐湿性 (%)	耐光性 (%)	最大濃度
						23°C/20%	30°C/80%				
2-1	比較例	5.7	39.0	26.0	63.6	+6.5	-5.0	86.2	+22	70	2.02
2-2	本発明	4.8	38.5	26.5	84.1	+7.0	-6.5	91.2	+6	69	2.01
2-3	本発明	4.2	38.0	25.5	64.3	+7.5	-6.5	94.4	+2	68	2.01
2-4	本発明	3.7	38.5	26.0	63.7	+6.5	-5.0	96.2	+2	68	1.97
2-5	比較例	2.8	38.5	24.5	64.2	+7.5	-6.5	97.3	+2	64	1.65

[0167] Also when a cation mordant is changed into instantiation mordant Mor-4 which are a cation monomer homopolymer from the result of Table 2, it turns out that the same effectiveness as an example -1 is acquired.

[0168] Although a curl property falls a little as compared with instantiation mordant Mor-1 when instantiation mordant Mor-4 are used, a water resisting property and moisture resistance are improving.

[0169] While the mean particle diameter of an example-3 <production of coating liquid 3-1> primary particle added 100ml of pure water to 900ml of 20% colloidal silica water solutions which are about 20nm and agitated with the high-speed homogenizer, 150ml of 25% water solutions of instantiation mordant Mor-1 was added, the high-speed homogenizer distributed for 30 more minutes, and pale clear dispersion liquid were obtained. Next, average degree of polymerization added 2ml for 10% polyvinyl alcohol water solution whenever [saponification / whose] is 88% by 300, and average degree of polymerization added gradually further 650ml (ethyl acetate is contained 4% of the weight) of 5% polyvinyl alcohol water solutions whenever [saponification / whose] is 88% by 3500. Subsequently, 40ml of borated water solutions was added 4% as a hardening agent, and 20ml ethanol was added, and the coating liquid 3-1 which adds 50ml of gelatin water solutions 10%, and forms the ink absorption layer of an opening mold further was produced.

<Production of the record form 3-1 to 3-5> Using the above-mentioned coating liquid 3-1, like the example -1, it dried and the record form 3-1 which has spreading and the film surface pH shown in Table 3 was produced on the base material used in the example -1. Furthermore, the record form 3-2 to 3-5 to which the film surface pH was changed like the example -1 so that it might become as [show / in Table 3] was produced.

[0170] About the obtained record form 3-1 to 3-5, void volume, ink absorptivity, glossiness, curl, a water resisting property, moisture resistance, lightfastness, and maximum density were evaluated like the example -1. The obtained result is shown in Table 3.

[0171]

[Table 3]

記録用紙		表面pH	空隙容量	インク吸収性	光沢度	カール (mm)		耐水性 (%)	耐湿性 (%)	耐光性 (%)	最大濃度
						23°C/20%	30°C/80%				
3-1	比較例	5.4	31.0	19.5	57.3	+3.5	-3.5	80.1	+32	62	2.17
3-2	本発明	4.8	31.5	20.0	58.3	+3.0	-3.5	86.2	+9	61	2.15
3-3	本発明	4.1	32.0	20.0	57.8	+3.5	-3.5	88.3	+6	61	2.15
3-4	本発明	3.5	31.5	19.5	57.4	+2.5	-4.0	89.5	+4	63	2.13
3-5	比較例	2.5	31.0	19.5	57.2	+3.5	-3.5	90.7	+4	62	1.82

[0172] Although void volume falls when it replaces with the silica compounded by the gaseous-phase method and colloidal silica is used from the result shown in Table 3, it turns out that a water resisting property and moisture resistance are improved without the record form 3-2 to 3-4 which set the film surface pH to 3-5 like the example -1 reducing the maximum concentration.

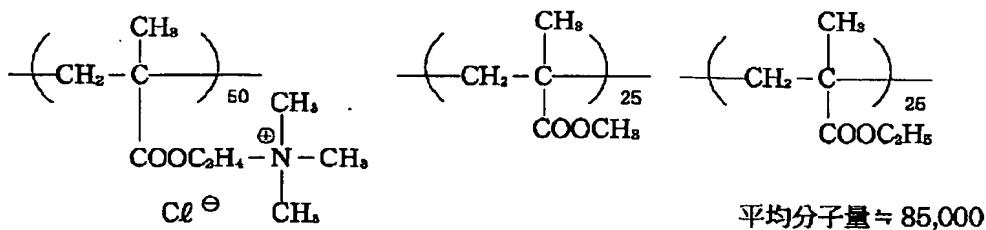
[0173] It replaced with the particle silica powder compounded by the gaseous-phase method the mean particle diameter of a 41st [-] example particle is about 7nm, and the record form 4-1 to 4-3 as well as the record form 1-3 of an example -1 was produced except having used the particle silica powder compounded by the gaseous-phase method the mean particle diameter of a primary particle is 12nm, 20nm, and 50nm.

[0174] Moreover, it is the following mordant about instantiation mordant Mor-1. - The record form 4-4 and 4-5 were produced like the record form 1-3 of an example -1 except having changed into A and -B.

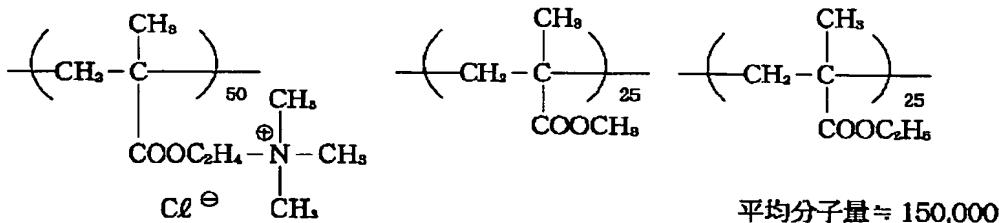
[0175]

[Formula 9]

媒染剤 $\leftarrow \text{A}$



媒染剤 - B



The film surface pH of the obtained record form 4-1 to 4-5 is shown in Table 4.

[0176] Moreover, void volume, ink absorptivity, glossiness, curl, a water resisting property, moisture resistance, lightfastness, and maximum density were evaluated like the example -1 about the obtained record form 4-1 to 4-5. The obtained result is shown in Table 4.

[0177]

[Table 4]

記録用紙		膜面pH	空隙容量	インク吸収性	光沢度	カール (mm)		耐水性 (%)	耐湿性 (%)	耐光性 (%)	最大密度
						23°C/20%	30°C/80%				
4-1	本発明	4.1	36.5	22.0	62.7	+3.5	-3.5	91.3	+6	71	2.03
4-2	本発明	4.0	35.0	22.5	59.2	+2.0	-3.0	93.7	+4	70	2.01
4-3	本発明	4.1	32.0	21.5	48.2	+2.0	-3.5	95.2	+4	68	1.96
4-4	本発明	4.0	37.5	24.5	42.3	+3.5	-4.0	92.5	+4	70	2.01
4-5	本発明	4.1	38.5	23.0	31.4	+3.0	-3.0	93.1	+4	68	1.99

[0178] As shown in Table 4, it has a high water resisting property and high moisture resistance, without neither of the record form 4-1 to 4-5 reducing curl, lightfastness, and the maximum concentration.

[0179] Moreover, if the mean particle diameter of the primary particle of the particle silica powder compounded by the gaseous-phase method increases, void volume and glossiness will fall gradually, and it turns out that the mean particle diameter of the primary particle of a desirable silica is about 30nm or less.

[0180] Moreover, when what has molecular weight high as a mordant is used, it turns out that gloss falls gradually. The minute aggregate has occurred in the coating liquid used for producing the record form 4-4 and 4-5, and this caused the gloss fall.

[0181] The record form 5-1 to 5-4 as well as the record form 1-3 of an example -1 was produced except having changed the ratio of the particle silica (silica) compounded by the example-5 gaseous-phase method, and polyvinyl alcohol (PVA), as shown in Table 5.

[0182] The film surface pH of the obtained record form 5-1 to 5-4 is shown in Table 4.

[0183] Moreover, void volume, ink absorptivity, glossiness, curl, a water resisting property, moisture resistance, lightfastness, and maximum density were evaluated like the example -1 about the obtained record form 5-1 to 5-4. The obtained result is shown in Table 5.

[0184] Moreover, the film surface pH of the record form 1-3, void volume, ink absorptivity, glossiness, curl, a water resisting property, moisture resistance, lightfastness, and maximum density were shown in Table 5 for reference.

[0185]

[Table 5]

記録用紙	(シリカ/PVA)比	膜面pH	空隙容量	インク吸収性	光沢度	カール (mm)		耐水性 (%)	耐湿性 (%)	耐光性 (%)	最大濃度	
						23°C/20%	30°C/80%					
1-3	本発明	7.2	4.0	37.5	23.5	63.3	+3.5	-3.0	90.4	+4	70	2.05
5-1	本発明	10.5	3.9	40.5	28.5	42.2	+5.0	-5.5	93.2	+7	64	1.97
5-2	本発明	5.0	4.0	34.5	19.5	66.5	+3.0	-2.0	89.3	+4	72	2.05
5-3	本発明	3.0	4.1	31.0	14.0	69.2	+2.0	-1.5	87.4	+4	74	2.09
5-4	本発明	1.5	4.0	23.0	10.5	73.2	+2.0	-1.5	86.3	+4	78	2.11

[0186] As shown in Table 5, it has a high water resisting property and high moisture resistance, without neither of the record form 5-1 to 5-4 reducing curl, lightfastness, and the maximum concentration.

[0187] Although void volume becomes large and ink absorptivity is improved, a minute crack generates the record form 5-1 which made ten or more the ratio to the polyvinyl alcohol of the particle silica powder compounded by the gaseous-phase method on the whole surface, and gloss is falling. Moreover, void volume is falling in the record form 5-4 which made two or less the ratio to the polyvinyl alcohol of the particle silica powder compounded by the gaseous-phase method.

[0188] The coating liquid 6-1 containing the component below per [example-6 <production of coating liquid 6-1> coating liquid 1L] was produced.

[0189]

Acid-treatment gelatin 38g Polyvinyl pyrrolidone (K-90) 12g Polyethylene oxide (average molecular weight = about 150,000) 10g Mordant (instantiation mordant Mor-15) 32g Cationic fluorescent brightener 0.1g Hardening agent (H-1):(H-1) pentane [1 and 5-diglycidyl-3-hydroxy] <production of the record form 6-1> 0.2g the obtained coating liquid 6-1 The paper base material which covered both sides of the stencil paper for photographs of 150 g/m² with polyethylene (the polyethylene layer which contains an anatase mold titanium dioxide with a thickness of 35 micrometers 13% of the weight is formed in the recording surface side) A polyethylene layer with a thickness of 25 micrometers should be formed in a rear-face side, and let on it the silica gelatin 2.2g and whose mean particle diameter are about 2 micrometers be a mat agent. The back layer contained two times 0.1 g/m is formed. After applying and carrying out a cooling set so that humid thickness may turn to 120 micrometers at a recording surface side, it dried and the record form 6-1 was obtained.

[0190] The film surface pH of the obtained record form 6-1 is shown in Table 6.

<Production of the record form 6-2 to 6-5> pH of coating liquid 6-1 was changed using the nitric acid or the sodium hydroxide, and the record form 6-2 to 6-5 as well as the record form 6-1 was produced.

[0191] The film surface pH of the obtained record form 6-2 to 6-5 is shown in Table 6.

[0192] Moreover, glossiness, curl, a water resisting property, moisture resistance, lightfastness, and maximum density were evaluated like the example-1 about the obtained record form 6-1 to 6-5. The obtained result is shown in Table 6.

[0193]

[Table 6]

記録用紙	膜面pH	光沢度	カール (mm)		耐水性 (%)	耐湿性 (%)	耐光性 (%)	最大濃度	
			23°C/20%	30°C/80%					
6-1	比較例	5.4	62.0	+8.0	-6.0	84.7	+19	79	2.12
6-2	本発明	4.6	62.7	+7.5	-6.5	87.1	+8	77	2.13
6-3	本発明	4.1	63.3	+9.0	-7.0	89.2	+4	78	2.15
6-4	本発明	3.6	61.8	+8.5	-6.5	90.5	+4	77	2.12
6-5	比較例	2.5	63.6	+8.5	-7.0	92.1	+2	76	1.53

The result of Table 6 shows that the same effectiveness as the ink absorption layer of an opening mold is acquired even if it is the case where an ink absorption layer is a swelling mold.

[0194] Except that the amount of example-of comparison 1 instantiation mordant Mor-1 is changed as shown in Table 7, and it was made for a film surface pH to come to show in Table 7, the record form 7-1 to 7-3 as well as the record form 1-1 of an example-1 was produced. In addition, it was made for the coverage of the particle silica powder compounded by the gaseous-phase method and polyvinyl alcohol to become fixed. Therefore, it follows on making the amount of instantiation mordant Mor-1 increase, and thickness is thick.

[0195] The film surface pH of the obtained record form 7-1 to 7-3 is shown in Table 7.

[0196] About the obtained record form 7-1 to 7-3, void volume, ink absorptivity, glossiness, curl, a water resisting property, moisture resistance, lightfastness, and maximum density were evaluated like the example -1. The obtained result is shown in Table 7.

[0197] Moreover, the amount of mordants of the record form 1-1, a film surface pH, void volume, ink absorptivity, glossiness, curl, a water resisting property, moisture resistance, lightfastness, and maximum density were shown in Table 7 for reference.

[0198]

[Table 7]

記録用紙	媒染剂量 (ml)	膜面 pH	空隙容量	インク 吸収性	光沢度	カール (mm)		耐水性 (%)	耐湿性 (%)	耐光性 (%)	最大密度	
						23°C / 20%	30°C / 80%					
1-1	比較例	100	5.5	38.0	24.0	62.0	+3.0	-3.0	83.4	+25	72	2.09
7-1	比較例	150	5.6	36.5	22.5	63.2	+9.5	-6.5	87.0	+21	60	2.08
7-2	比較例	200	5.6	36.0	20.5	63.7	+14.5	-10.0	91.3	+15	51	2.06
7-3	比較例	300	5.7	32.5	18.0	64.1	+21.0	-15.0	92.2	+11	37	2.08

[0199] As shown in Table 7, even when a film surface pH is five or more, if the quantity of the amount of a cation mordant is increased, a water resisting property and moisture resistance will improve greatly, but when it is made five or less film surface pH, moisture resistance cannot be improved to like. Moreover, if the quantity of the amount of a cation mordant is increased, curl will become large and lightfastness will get worse rapidly.

[Translation done.]

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[Procedure amendment 1]

[Document to be Amended] Specification

[Item(s) to be Amended] Claim

[Method of Amendment] Modification

[Proposed Amendment]

[Claim(s)]

[Claim 1] The ink jet record form characterized by for at least one-layer ink absorption layer prepared on the hydrophobic base material having contained the non-subtlety particle in the cation mordant and list which have mordacity to a hydrophilic binder and an anionic color, and forming the opening, containing a hardening agent further, and making the film surface pH by the side of the recording surface of an ink absorption layer into 3 or more and 5 or less.

[Claim 2] The ink jet record form according to claim 1 with which said hydrophilic binder is characterized by being polyvinyl alcohol and its derivative.

[Claim 3] The ink jet record form according to claim 1 or 2 with which said non-subtlety particle is characterized by the mean particle diameter of a primary particle being a non-subtlety particle 30nm or less.

[Claim 4] The ink jet record form according to claim 1 to 3 with which said hardening agent is characterized by being a way acid or way sand.

[Claim 5] The weight ratio to said hydrophilic binder of said non-subtlety particle is an ink jet record form according to claim 1 to 4 characterized by being 2-10.

[Claim 6] The ink jet record form according to claim 1 to 5 characterized by said non-subtlety particles being at least one sort of non-subtlety particles chosen from the silica compounded by the gaseous-phase method, colloidal silica, an alumina, and hydrated alumina.

[Claim 7] The ink jet record form according to claim 1 to 6 with which said cation mordant is characterized by being a with an average molecular weight of 50,000 or less water-soluble mordant.

[Claim 8] The ink jet record form according to claim 1 to 7 with which the amount of said cation mordant is characterized by being 0.01-0.3 in a weight ratio to a non-subtlety particle.

[Claim 9] The ink jet record approach that pH is characterized by what is recorded with the recording ink it is

[recording ink] 3 or more and 8 or less at an ink jet record form according to claim 1 to 8.

[Procedure amendment 2]

[Document to be Amended] Specification

[Item(s) to be Amended] 0024

[Method of Amendment] Modification

[Proposed Amendment]

[0024]

[Means for Solving the Problem] The above-mentioned purpose of this invention,

(1) The ink jet record form characterized by for at least one-layer ink absorption layer prepared on the hydrophobic base material having contained the non-subtlety particle in the cation mordant and list which have mordacity to a hydrophilic binder and an anionic color, and forming the opening, containing a hardening agent further, and making the film surface pH by the side of the recording surface of an ink absorption layer into 3 or more and 5 or less.

(2) An ink jet record form given in the above (1) said whose hydrophilic binder is characterized by being polyvinyl alcohol and its derivative.

(3) The above (1) said whose non-subtlety particle is characterized by the mean particle diameter of a primary particle being a non-subtlety particle 30nm or less, or an ink jet record form given in (2).

(4) An ink jet record form given in either of above-mentioned (1) – (3) to which said hardening agent is characterized by being a way acid or way sand.

(5) The weight ratio to said hydrophilic binder of said non-subtlety particle is an ink jet record form given in either of above-mentioned (1) – (4) characterized by being 2–10.

(6) said —less — subtlety — a particle — a gaseous phase — a method — compounding — having had — a silica — colloidal silica — an alumina — and — hydrated alumina — inside — from — choosing — having had — at least — one — a sort —less — subtlety — a particle — it is — things — the description — ** — carrying out — the above — (— one —) – (— five —) — either — a publication — an ink jet — record — a form .

(7) An ink jet record form given in either of above-mentioned (1) – (6) to which said cation mordant is characterized by being a with an average molecular weight of 50,000 or less water-soluble mordant.

(8) An ink jet record form given in either of above-mentioned (1) – (7) to which the amount of said cation mordant is characterized by being 0.01–0.3 in a weight ratio to a non-subtlety particle.

(9) The above (1) The ink jet record approach that pH is characterized by what is recorded with the recording ink it is [recording ink] 3 or more and 8 or less at an ink jet record form given in either of – (8). It is alike and is attained more.

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(54)【発明の名称】 インクジェット記録用紙及びインクジェット記録方法

(57)【要約】

【課題】 少ないカチオン媒染剤の使用量で高い耐水性
と耐湿性が達成できるインクジェット記録用紙を提供す
ること。

【解決手段】 親水性バインダー及びアニオン性染料に
対して媒染力を有するカチオン媒染剤を含有するインク
吸収層を支持体上に少なくとも1層有し、インク吸収層
の記録面側の膜面pHを3以上、5以下としたインクジ
ェット記録用紙及びpHが3以上、8以下である記録液
で記録するインクジェット記録方法。

【特許請求の範囲】

【請求項1】 親水性バインダー及びアニオン性染料に対して媒染力を有するカチオン媒染剤を含有するインク吸收層を支持体上に少なくとも1層有し、インク吸收層の記録面側の膜面pHを3以上、5以下としたことを特徴とするインクジェット記録用紙。

【請求項2】 インク吸收層が、1次粒子の平均粒径が30nm以下の無機微粒子を含有し、空隙が形成されていることを特徴とする請求項1に記載のインクジェット記録用紙。

【請求項3】 無機微粒子が、気相法により合成されたシリカ、コロイダルシリカ及びアルミナ及びアルミナ水和物の中から選ばれた少なくとも1種の無機微粒子であることを特徴とする請求項2に記載のインクジェット記録用紙。

【請求項4】 カチオン媒染剤が、平均分子量が5万以下の水溶性媒染剤であることを特徴とする請求項1～3のいずれかに記載のインクジェット記録用紙。

【請求項5】 カチオン媒染剤の量が、無機微粒子に対して、重量比で0.01～0.3であることを特徴とする請求項1～4のいずれかに記載のインクジェット記録用紙。

【請求項6】 親水性バインダーが、ポリビニルアルコールであることを特徴とする請求項1～5のいずれかに記載のインクジェット記録用紙。

【請求項7】 インク吸收層がほう酸またはほう砂を含有することを特徴とする請求項6に記載のインクジェット記録用紙。

【請求項8】 支持体が、非吸水性支持体であることを特徴とする請求項1～7のいずれかに記載のインクジェット記録用紙。

【請求項9】 請求項1～8のいずれかに記載のインクジェット記録用紙に、pHが3以上、8以下である記録液で記録することを特徴とするインクジェット記録方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、水溶性染料を含有するインクを用いて画像を記録するインクジェット記録用紙に関し、更に詳しくは、記録後の画像の耐水性や耐湿性を改良したインクジェット記録用紙に関する。

【0002】

【従来の技術】インクジェット記録は、インクの微小液滴を種々の作動原理により飛翔させて紙などの記録シートに付着させ、画像・文字などの記録を行うものであるが、比較的高速、低騒音、多色化が容易である等の利点を有している。この方式で従来から問題となっていたノズルの目詰まりとメンテナンスについては、インク及び装置の両面から改良が進み、現在では各種プリンター、ファクシミリ、コンピューター端末等さまざまな分野で急速に普及している。

【0003】その詳細は、例えば、インクジェット記録技術の動向（中村孝一編、平成7年3月31日、日本科学情報株式会社発行）に記載されている。

【0004】このインクジェット記録方式で使用される記録用紙としては、印字ドットの濃度が高く、色調が明るく鮮やかであること、インクの吸収が早く印字ドットが重なった場合に於いてもインクが流れ出したり滲んだりしないこと、印字ドットの横方向への拡散が必要以上に大きくなく、かつ周辺が滑らかでなければいけないこと等が一般的には要求されている。

【0005】インクジェット記録用紙としては、従来から種々の記録用紙が用いられている。例えば、普通紙、親水性バインダーと無機顔料から成る層を塗設した各種の塗工紙（アート紙、コート紙、キャストコート紙等）、更には、両面をプラスチック樹脂で被覆した各種の紙、透明または不透明の各種のプラスチックフィルムよりなる支持体上に記録層としてインク吸収層を塗設したインクジェット記録用紙が用いられている。

【0006】上記インク吸収層は、親水性バインダーを主体に構成された膨潤型のインク吸収層、記録層中に空隙を設けた空隙型のインク吸収層に大きく分けられる。

【0007】膨潤型のインク吸収層は、親水性バインダーの膨潤作用でインクを保持するものであり、親水性バインダーとしては、例えば、ゼラチン、ポリビニルアルコール、ポリエチレンオキサイド、ポリビニルピロリドン、フルラン、カルボキシメチルセルロース、ヒドロキシエチルセルロース、デキストラン、デキストリン、ポリアクリル酸及びその塩、寒天、 κ -カラギーナン、 λ -カラギーナン、 ι -カラギーナン、キサンテンガム、ローカストビーンガム、アルギン酸、アラビアゴム、特開平7-195826号公報及び同7-9757号公報に記載のポリアルキレンオキサイド系共重合ポリマー、水溶性ポリビニルブチラール、あるいは、特開昭62-245260号公報に記載のカルボキシル基やスルホン酸基を有するビニルモノマーの単独重合体や共重合体等が、単独あるいは2種以上を組み合わせて用いられる。

【0008】空隙型のインク吸収層は、層に形成された空隙にインクを保持するものであり、通常、空隙は、各種の無機固体微粒子や有機の固体微粒子を皮膜中に含有させることによって形成している。

【0009】上記の目的で用いられる無機微粒子としては、例えば、軽質炭酸カルシウム、重質炭酸カルシウム、炭酸マグネシウム、カオリン、クレー、タルク、硫酸カルシウム、硫酸バリウム、二酸化チタン、酸化亜鉛、水酸化亜鉛、硫化亜鉛、炭酸亜鉛、ハイドロタルサイト、珪酸アルミニウム、ケイソウ土、珪酸カルシウム、珪酸マグネシウム、合成非晶質シリカ、コロイダルシリカ、アルミナ、コロイダルアルミナ、擬ペーマイト、水酸化アルミニウム、リトポン、ゼオライト、水酸化マグネシウム等の白色無機顔料等が挙げられる。

【0010】これらの無機微粒子は、1次粒子のままでバインダー中に均一に分散させても、また、2次凝集粒子を形成してバインダー中に均一に分散させてもよい。

【0011】有機微粒子としては、例えば、ポリスチレン、ポリアクリル酸エステル類、ポリメタクリル酸エステル類、ポリアクリルアミド類、ポリエチレン、ポリプロピレン、ポリ塩化ビニル、ポリ塩化ビニリデン、または、これらの共重合体、尿素樹脂、メラミン樹脂等の微粒子が挙げられる。

【0012】インクジェット記録法において、記録液に水溶性の染料を使用した場合、高い彩度のカラー画像が得られるが、耐水性や耐湿性が劣っている。これに対して、記録液に顔料を使用した場合、耐水性や耐湿性の点で優れているが、色材の分光吸収特性がブロードで高い彩度の色素画像が得られにくい。

【0013】耐水性や耐湿性が劣っている水溶性の染料を使用した記録液を使用した場合の耐水性や耐湿性を改良するために、従来から色素を固定させる種々の方法が提案されている。

【0014】これら提案の中で耐水性や耐湿性を改良する有効な手段は、3級または4級の窒素原子を有するカチオン性ポリマーの均一な水溶液や微粒子ラテックスを用いる方法である。

【0015】従来、インクジェット記録法やインクジェット記録用紙としては、例えば、特開昭57-36692号公報に、原紙やポリエチレンテレフタレートフィルム支持体上に、ゼラチン及び塩基性媒染剤を含有する塗布液を塗設しインク受容層としたインクジェット記録用紙が、特開昭53-49113号公報に、紙内にポリエチレンイミンを含浸させた水性インキ記録用紙が、特開昭58-24492号公報に、カチオンまたはアニオン基を有する電解質ポリマーを有する記録材が、特開昭63-224988号に、第1級ないし第3級アミンまたは第4級アンモニウム塩を含有し、pHを2~8としたインク受容層を有する被記録材料が、特開昭63-307979号公報に、3級または4級窒素原子を有する親水性ポリマー媒染剤と親水性基を有する重合体を含有する層を設けたインクジェット記録シートが、特開昭59-198186号公報及び同59-198188号公報に、ポリエチレンイミンの有機塩基を基材中または基材上の塗工層中に含有させた被記録材料が、特開昭60-46288号公報に、特定染料を含有するインクとポリアミン等を含有する記録材料を用いたインクジェット記録法が、特開昭61-61887号公報、同61-72581号公報、同61-252189号公報及び同62-174184号公報に、ポリアリルアミンを含有するインクジェット記録用紙が、特開昭61-172786号公報に、分子間水素結合を有するポリマー（ゼラチン、ポリエチレニミン等）と分子間に水素結合性基を有しないポリマー（ポリエチレングリコール、ポリビニルピロリドン等）を含有する層を有するインクジェット記録材料が、特開昭63-162275号公報に、カチオン性ポリ

マーとカチオン性界面活性剤を支持体上に塗布または含浸させたインクジェット記録用紙が、特開平6-143798号公報に、プラスチック支持体上に第4級アンモニウム塩重合物とカチオン変成ポリビニルアルコールを主成分とする染料定着層とその上に設けられた染料透過・インク吸収層を有する記録シートが記載されている。

【0016】更に、特開昭59-20696号公報、同59-33176号公報、同59-33177号公報、同59-96987号公報、同59-155088号公報、同60-11389号公報、同60-49990号公報、同60-83882号公報、同60-109894号公報、同61-277484号公報、同61-293886号公報、同62-19483号公報、同62-18493号公報、同63-49478号公報、同63-115780号公報、同63-203896号公報、同63-274583号公報、同63-280681号公報、同63-260477号公報、特開平1-9776号公報、同1-24784号公報、同1-40371号公報、同3-133686号公報、同6-234268号公報、同7-125411号公報等には、特定の3級または4級の窒素原子を有するポリマーまたは化合物をインク受容層中に添加することが記載されている。

【0017】かかる先行技術に記載されている染料を固定する技術は、染料の固定という点からはそれなりの効果を認められるが、必ずしも充分ではない。

【0018】カチオン性の媒染剤を用いて耐水性や耐湿性を高めるためには媒染剤の使用量を増せばよいが、この場合カチオン媒染剤の增量に伴う種々の欠点が生じやすい。

【0019】例えば、カチオン媒染剤は、記録後の染料の耐光性を劣化させたり、保存中にイエロー着色を起こしやすい傾向があり、媒染剤の添加量の増大に伴いこうした欠点が顕著になりやすい。

【0020】更に、カチオン媒染剤として水溶性媒染剤を用いた場合には、添加量の増大に伴いカールを増加させたり、皮膜の造膜性を劣化させたり、脆弱性をもたらすという欠点がある。インク吸収層が膨潤型のものである場合には、特に後者の問題が大きく、媒染剤の添加量の増大させると、他の親水性バインダーとの相溶性が悪化して造膜性や脆弱性を劣化させる。また、インク吸収層が空隙型のものである場合には、空隙層を厚膜にしなければならないため、媒染剤の添加量が増大し、カールが生じやすくなる。

【0021】また、カチオン媒染剤として乳化重合されたラテックス粒子を用いた場合、インク吸収層が膨潤型のものであるときには、添加量の増大に伴い皮膜の失透やクツツキが生じやすくなり、また、インク吸収層が空隙型のものであるときには、空隙を塞いで空隙容量を低下させてしまう。

【0022】上記問題点について検討したところ、インク吸収層の記録面側の膜面のpH値を特定の値とすることにより解決できることが判明した。

【0023】

【本発明が解決しようとする課題】本発明は上記の実態

に鑑みてなされたものであって、本発明の第1の目的は、少ないカチオン媒染剤の使用量で高い耐水性と耐湿性が達成できるインクジェット記録用紙を提供することにある。第2の目的は、カチオン媒染剤の使用によってもたらされる前記の種々の欠点を抑制したインクジェット記録用紙を提供することにある。

【0024】

【課題を解決するための手段】本発明の上記目的は、

(1) 親水性バインダー及びアニオン性染料に対して媒染力を有するカチオン媒染剤を含有するインク吸収層を支持体上に少なくとも1層有し、インク吸収層の記録面側の膜面pHを3以上、5以下としたことを特徴とするインクジェット記録用紙。

(2) インク吸収層が、1次粒子の平均粒径が30nm以下の無機微粒子を含有し、空隙が形成されていることを特徴とする上記(1)に記載のインクジェット記録用紙。

(3) 無機微粒子が、気相法により合成されたシリカ、コロイダルシリカ及びアルミナ及びアルミナ水和物の中から選ばれた少なくとも1種の無機微粒子であることを特徴とする上記(2)に記載のインクジェット記録用紙。

(4) カチオン媒染剤が、平均分子量が5万以下の水溶性媒染剤であることを特徴とする上記(1)～(3)のいずれかに記載のインクジェット記録用紙。

(5) カチオン媒染剤の量が、無機微粒子に対して、重量比で0.01～0.3であることを特徴とする上記(1)～(4)のいずれかに記載のインクジェット記録用紙。

(6) 親水性バインダーが、ポリビニルアルコールであることを特徴とする上記(1)～(5)のいずれかに記載のインクジェット記録用紙。

(7) インク吸収層がほう酸またはほう砂を含有することを特徴とする上記(6)に記載のインクジェット記録用紙。

(8) 支持体が、非吸水性支持体であることを特徴とする上記(1)～(7)のいずれかに記載のインクジェット記録用紙。

(9) 上記(1)～(8)のいずれかに記載のインクジェット記録用紙に、pHが3以上、8以下である記録液で記録することを特徴とするインクジェット記録方法。により達成される。

【0025】先に、先行技術として示した特開昭63-224988号公報には、第1級～第3級アミン若しくは第4級アンモニウム塩を含有しインク受容層のpHを2～8の範囲内に調整することで媒染剤に伴う臭気の発生を抑制した被記録材が記載されているが、インク吸収層の記録面側の膜面pHを特定のpH値とすることにより耐水性と耐湿性が得られることについては記載されていない。また、該公報には、インク吸収層の記録面側の膜面pHを3～5の範囲とした実施例も記載されておらず、膜面pHとして特定化された3～5の範囲を選定することを

示唆する記載もない。しかも、インク受容層のpHが2～8の範囲にあっても、インク吸収層の記録面側の膜面pHが3～5でない場合には本発明の効果は得られない。

【0026】従って、本発明は、上記先行技術とは目的を異にし、しかも、構成も異なるものである。

【0027】以下、本発明を詳細に説明する。

【0028】本発明において、支持体としては、従来からインクジェット記録用紙に用いられる支持体、例えば、普通紙、アート紙、コート紙及びキャストコート紙等の紙支持体、プラスチック支持体、両面をポリオレフィンで被覆した紙支持体、これらを貼り合わせた複合支持体を用いることができる。

【0029】高い光沢性、記録後の高い平滑性と最高濃度を得ることを希望する場合には、非吸水性支持体を用いることが好ましい。非吸水性支持体としては、プラスチックフィルムよりなる支持体またはポリオレフィンで両面を被覆した紙支持体が好ましく用いられ、ポリオレフィンで両面を被覆した紙支持体が最も好ましいものとして用いられる。

【0030】プラスチックフィルムよりなる支持体としては、例えば、ポリエチレンフィルム、ポリプロピレンフィルム、ポリスチレンフィルム、ポリエチレンテレフタレートフィルム、ポリエチレンナフタレートフィルム、トリアセチルセルロースフィルム、ポリ塩化ビニルフィルム、ポリイミドフィルム、ポリカーボネートフィルム、セロファンなどのプラスチックフィルムよりなる支持体等が好ましく用いられる。

【0031】これらのプラスチックフィルムは透明なもの、半透明なもの及び不透明なものを用途に応じて適宜使い分けることができる。

【0032】支持体には、白色のプラスチックフィルムを用いることも好ましい。白色のフィルムとしては、少量の硫酸バリウム、酸化チタン、酸化亜鉛などの白色顔料をプラスチックに含有させたフィルム、裏面側またはインク吸収層側に、白色顔料(酸化チタン、硫酸バリウムなど)を有する層を設けたフィルムを用いることができる。

【0033】ポリオレフィンで両面を被覆した紙支持体の原紙は、木材パルプを主原料とし、必要に応じて、ポリプロピレンなどの合成パルプあるいはナイロンやポリエステルなどの合成繊維を加えて抄紙される。木材パルプとしては、LBKP、LBSP、NBKP、NBS P、LDP、NDP、LUKP、NUKPのいずれも用いることができるが、短纖維分の多いLBKP、NBS P、LBSP、NDP、LDPをより多く用いることが好ましい。但し、LBSP及びまたはLDPの比率は10重量%以上、70重量%以下が好ましい。

【0034】パルプは、不純物の少ない化学パルプ(例えば、硫酸塩パルプ、亜硫酸塩パルプ)が好ましく、ま

た、漂白処理を行って白色度を向上させたパルプも有用である。

【0035】原紙中には、高級脂肪酸、アルキルケンダイマー等のサイズ剤、炭酸カルシウム、タルク、酸化チタンなどの白色顔料、スターチ、ポリアクリルアミド、ポリビニルアルコール等の紙力増強剤、蛍光増白剤、ポリエチレングリコール類等の水分保持剤、分散剤、4級アンモニウム塩等の柔軟化剤などを適宜添加することができる。

【0036】抄紙に使用するパルプの濾水度は、CSFの規定で200～500ccが好ましく、また、叩解後の纖維長がJIS-P-8207に規定される24メッシュ残分の重量%と42メッシュ残分の重量%との和が30乃至70%が好ましい。なお、4メッシュ残分の重量%は20重量%以下であることが好ましい。

【0037】原紙の坪量は60乃至250gが好ましく、特に、90乃至200gが好ましい。原紙の厚さは50乃至250μmが好ましい。

【0038】原紙は抄紙段階または抄紙後にカレンダー処理をして高平滑性を与えることができる。原紙密度は0.7乃至1.2g/m² (JIS-P-8118) が一般的である。更に原紙剛度はJIS-P-8143に規定される条件で20乃至200gが好ましい。

【0039】原紙表面には表面サイズ剤を塗布してもよく、表面サイズ剤としては前記原紙中に添加できるサイズ剤と同様のサイズ剤を使用できる。

【0040】原紙のpHは、JIS-P-8113で規定された熱水抽出法により測定された場合、5～9であることが好ましい。

【0041】原紙表面及び裏面を被覆するポリオレフィンとしては、ポリエチレンが特に好ましく、低密度のポリエチレン (LDPE)、高密度のポリエチレン (HDPE) が用いられるが、他の線状低密度ポリエチレン (LLDPE) やポリプロピレン等も使用することができる。

【0042】インク吸収層側のポリエチレン層は、写真用印画紙で広く行われているように、ポリエチレン中にルチルまたはアナーチ型の酸化チタンを添加して不透明度及び白色度を改良したものが好ましい。酸化チタンの含有量はポリエチレンに対して概ね3～20重量%、好ましくは5～15重量%である。

【0043】原紙の表裏のポリエチレンの使用量は、インク吸収層やバック層を設けた後、低湿及び高湿化で保存されたときにカールがないように選択される。通常、インク吸収層側のポリエチレン層の厚さを20～50μm、バック層側のポリエチレン層の厚さを10～40μmの範囲とする。

【0044】本発明において、以下の特性を有しているポリエチレン被覆紙支持体を好ましく用いることができる。

① 引張り強さ：JIS-P-8113で規定される強度で縦方向が2乃至30kg、横方向が1乃至20kg

②引き裂き強度：JIS-P-8116による規定方法で縦方向が10乃至300g、横方向が20乃至400g

③クラーク剛度：20～400cm³/100

④圧縮弾性率：10³Kgf/cm²以上

⑤表面平滑度：JIS-P-8119に規定されるベック平滑度が500秒以上、特に1000秒以上

⑥表面粗さ：JIS-B-0610に規定された方法で測定された断面曲線からカットオフ値0.8mmの条件で導かれるろ波うねり曲線について、基準長2.5mmとしてろ波最大うねりを測定したときに、その任意の測定点100個で最大うねりが6μm以上の点が5個以内、また、10点平均粗さが4μm以内

⑦表面光沢度：JIS-Z-8741に規定された方法で75度の角度で測定した表面光沢度が30%以上、好ましくは70%以上、特に好ましくは90%以上

⑧表面白色度：JIS-Z-8722に記載された方法で測定し、JIS-Z-8729に従って表示したとき、L*は85%以上、特に90%以上、また、(a'*、b*)は(-2、2)、(4、2)、(4、-8)及び(-3、-8)で囲まれる範囲の色調にあること

⑨不透明度：JIS-P-8138に規定された方法で測定したときに50%以上、特に90%以上、最も好ましくは94%以上支持体には、記録層との接着強度を大きくする等の目的で、記録層の塗布に先立って、支持体にコロナ放電処理や下引処理等を行うことが好ましい。

【0045】本発明のインクジェット記録用紙は、支持体上に少なくとも1層のインク吸収層を有する。このインク吸収層は、膨潤型であっても、空隙型であってもよく、更に両者の層を支持体上の同一の側に設けたものであってもよい。

【0046】膨潤層はインク液滴が着弾した際にインク液滴を適度の広さに拡げると同時に膨潤してインク液滴を吸収する。この膨潤層に吸収されたインク中の水やその他の有機溶媒はその後徐々に蒸発していき、最終的には非揮発成分である染料のみが実質的に皮膜中に残される。

【0047】膨潤型のインク吸収層は、インク液滴に対して高い膨潤性を示すことが必要であり、インク液膨潤性を示す親水性バインダーが主たる構成成分として用いられる。好ましく用いられる親水性バインダーとしては、例えば、ゼラチンまたはゼラチン誘導体 (フェニルカルバモイル化ゼラチン等)、ポリビニルピロリドン (平均分子量が約20万以上が好ましい)、フルラン、ポリビニルアルコールまたはその誘導体、ポリエチレングリコール (平均分子量が10万以上が好ましい)、カルボキシメチルセルロース、ヒドロキシエチルセルロース、デキストラン、デキストリン、ポリアクリル酸及びその塩、寒天、 κ -カラギーナン、 λ -カラギーナン、 ι -

カラギーナン、キサンテンガム、ローカストビーンガム、アルギン酸、アラビアゴム、特開平7-195826号公報及び同7-9757号公報に記載のポリアルキレンオキサイド系共重合性ポリマー、水溶性ポリビニルブチラール、あるいは、特開昭62-245260号公報に記載のカルボキシル基やスルホン酸基を有するビニルモノマーの単独またはこれらのビニルモノマーを繰り返して有する共重合体等のポリマーを挙げることができる。これらの親水性バインダーは単独で使用してもよく、2種以上を併用してもよい。

【0048】膨潤型のインク吸収層はインク液に対する早い浸透性及び膨潤性を有していることが必要なために、膨潤型のインク吸収層の親水性バインダーには、分子量が20万以上のポリビニルピロリドン、分子量が約5万以上のポリエチレンオキサイド、分子量が10万以上のポリエチレンオキサイドとポリプロピレンオキサイドとの共重合体、ヒドロキシエチルセルロース及びポリアクリルアミドから選ばれる少なくとも1種を含有していることが好ましい。

【0049】安定高速塗布の観点からすると、可逆的にゾルゲル変換可能な親水性バインダーを一部使用するのが好ましく、この点から、ゼラチン、ゼラチン誘導体及び κ -カラギーナンの少なくとも1種を使用するのが好ましい。

【0050】膨潤型のインク吸収層に用いられるバインダーは、ゼラチンまたはゼラチン誘導体を少なくとも有するものが好ましい。特に好ましい膨潤型のインク吸収層は、バインダーとして、ゼラチンまたはゼラチン誘導体とポリビニルピロリドンの組み合わせ、ゼラチン誘導体とポリビニルアルコール及びその誘導体の組み合わせ、ゼラチン誘導体とポリビニルピロリドンとポリビニルアルコールの組み合わせ、ゼラチンまたはゼラチンとポリアルキレングリコール及びその誘導体の組み合わせのバインダーを用いたものである。

【0051】上記において好ましく用いられるゼラチンとしては、通常のアルカリ処理ゼラチン及び酸処理ゼラチンが挙げられる。ゼラチンは、等電点が9~5の範囲のものを適宜選択して用いることができる。

【0052】誘導体ゼラチンとしては、ゼラチンのアミノ基またはイミノ基を、無水フタル酸等の酸無水物やフェニルイソシアネート等のイソシアネート類等と反応させアミノ基及びイミノ基の少なくとも一部を不活性化させたゼラチンが好ましく用いられる。

【0053】インク吸収層が膨潤型である場合は、インク吸収層の乾燥膜厚は、概ね、4~20 μ m、好ましくは6~15 μ mの範囲である。

【0054】インク吸収層が空隙型の場合、空隙は、親水性または疎水性のバインダーと無機または有機の固体粒子との間に形成される。

【0055】空隙の形成は種々の方式で行うことができ

る。以下に代表的な空隙型のインク吸収層の形成方法について説明する。

【1】相分離する2種以上のポリマーを含有する均一な塗布液を支持体上に塗布し、乾燥過程でこれらのポリマーを相分離させて空隙を形成する方法。

【2】固体微粒子及び親水性または疎水性バインダーを含有する塗布液を支持体上に塗布し、乾燥後に、記録用紙を水或いは適当な有機溶媒を含有する液に浸漬して固体微粒子を溶解させて空隙を作成する方法。

【3】加熱発泡する性質を有する化合物を含有する塗布液を支持体上に塗布し、乾燥過程でこれらの化合物を発泡させて皮膜中に空隙を形成する方法。

【4】多孔質固体微粒子と親水性バインダーを含有する塗布液を支持体上に塗布し、多孔質微粒子中や多孔質微粒子間に空隙を形成する方法。

【5】親水性バインダーに対して、概ね等量以上の容積を有する固体微粒子及びまたは油滴微粒子を混合した塗布液を支持体上に塗布し、乾燥させて、親水性バインダーと固体微粒子、油滴微粒子の間に空隙を作成する方法。

【6】平均粒径が約0.1 μ m程度以下の固体微粒子を含有させた塗布液中の固体微粒子を、塗布液の調整時または皮膜形成時に凝集させ、2次粒子または3次元構造を形成させて空隙を作成する方法。

【0056】本発明の記録用紙における空隙形成方法は上記のいかなる手段によってもよいが、カチオン媒染剤を添加することが可能であり、表面のpHを3~5に調節することができる必要がある。また、記録紙表面の光沢度をあまり低下させず、低コストで作成する観点からすると、製造工程が複雑でない方法が好ましい。

【0057】以上の観点から、本発明を実施するに当たっての好ましい空隙を形成させる方法としては、上記【5】または【6】の方法が好ましく、特に好ましい方法は【6】の方法である。

【0058】空隙型のインク吸収層において、空隙の総量(空隙容量)は記録用紙1 m^2 当たり20ml以上あることが好ましい。

【0059】空隙容量が20ml/ m^2 未満である場合、印字時のインク量が少ない場合にはインク吸収性は良好であるものの、インク量が多くなるとインクが完全に吸収されず、画質を低下させたり、乾燥性が遅いなどの問題が生じやすい。

【0060】空隙容量の上限は特に制限されないが、空隙型のインク吸収層の膜厚を概ね50 μ m以下にすることがひび割れ等の皮膜の物理的特性を悪化させないために必要で、この点からすると空隙容量を40ml/ m^2 以下とすることは難しい。

【0061】本発明において、空隙容量は、J.T.A.P.P.I.紙パルプ試験方法 No.51-87 紙及び板紙の液体吸収性試験方法(プリストー法)に記載された方

法で測定した時、吸収時間2秒における液体転移量(ml/m^2)で表される。なお、上記の測定方法では、測定に純水(イオン交換水)が使用されているが、測定面積の判別を容易にするために、2%未満の水溶性染料を含有させてもよい。

【0062】空隙型のインク吸収層において、固体分容量に対する空隙容量を空隙率という。本発明において、空隙率を150%以上、特に、200%以上とすることが、不必要に膜厚を厚くせないで空隙を効率的に形成できるので好ましい。空隙率の上限は、皮膜の強度や造膜性から一般には制約を受けるが、通常は400%以内である。

【0063】固体微粒子を含有させて空隙型のインク吸収層を形成させる場合、固体微粒子としては従来インクジェット記録用紙で公知の各種の無機または有機の固体微粒子を用いることができる。

【0064】上記目的で用いられる無機微粒子の例としては、軽質炭酸カルシウム、重質炭酸カルシウム、炭酸マグネシウム、カオリン、クレー、タルク、硫酸カルシウム、硫酸バリウム、二酸化チタン、酸化亜鉛、水酸化亜鉛、硫化亜鉛、炭酸亜鉛、ハイドロタルサイト、珪酸アルミニウム、ケイソウ土、珪酸カルシウム、珪酸マグネシウム、合成非晶質シリカ、コロイダルシリカ、アルミナ、コロイダルアルミナ、擬ペーマイト、水酸化アルミニウム、リトポン、ゼオライト、水酸化マグネシウム等の白色無機顔料等を挙げることができる。

【0065】無機微粒子は、バインダー中に1次粒子のままで均一に分散されていてもよく、2次凝集粒子を形成してバインダー中に均一に分散されていてもよい。

【0066】有機微粒子の例としては、ポリスチレン、ポリアクリル酸エステル類、ポリメタクリル酸エステル類、ポリアクリルアミド類、ポリエチレン、ポリプロピレン、ポリ塩化ビニル、ポリ塩化ビニリデン、またはこれらの共重合体、尿素樹脂、またはメラミン樹脂等の微粒子が挙げられる。

【0067】本発明においては、高い空隙率が得られるという観点からすると無機微粒子が好ましい。

【0068】上記無機微粒子は、1次粒子の粒径が30nm以下のものを使用することが好ましい。特に好ましい無機微粒子の1次粒子の粒径は20nm以下である。

【0069】1次粒子の平均粒径が30nmを超える粒子を使用した場合、水溶性ポリマー型のカチオン媒染剤と凝集が起りやすくなり、形成した凝集粒子も粗大化して光沢性が低下してしまう。

【0070】1次粒子の粒径の下限は特に限定されないが、粒子の製造上の観点から概ね3nm以上、特に6nm以上である。

【0071】無機微粒子の平均粒径は、粒子そのものあるいは空隙型のインク吸収層の断面や表面に現れた粒子を電子顕微鏡で観察し、100個の任意の粒子の粒径を求めてその単純平均値(個数平均)として求められる。こ

こで個々の粒子の粒径はその投影面積に等しい円を仮定したときの直径で表したものである。

【0072】無機微粒子としては、1次粒子の平均粒径が30nm以下の無機微粒子と平均粒径が30nm以上の無機微粒子を併用することも可能であるが、この場合、30nmを超える無機微粒子の比率は全無機微粒子に対して50重量%以下とすることが好ましく、20重量%以下がより好ましい。

【0073】濃度の高い画像が形成される、鮮明な画像が記録できる、低コストで製造できる等の点からすると、固体微粒子としては、気相法により合成された微粒子シリカ、コロイダルシリカ及びアルミナまたはアルミニナ水和物から選ばれた固体微粒子を用いることが好ましい。

【0074】本発明において好ましく用いられるアルミナまたはアルミニナ水和物は、半径が3~10nmで、細孔容積の和が0.2~2ml/gである多孔質アルミナまたはその含水物である。細孔容積は、公知の窒素吸着法により測定することができる。

【0075】アルミナまたはアルミニナ水和物は、結晶性であっても、非晶質であってもよく、また、不定形粒子、球状粒子、針状粒子など任意の形状のものを使用することができる。

【0076】気相法により合成された微粒子シリカは、通常、四塩化珪素を水素及び酸素と共に高温で燃焼して得ることができ、1次粒子の粒子径が5~500nmのシリカ粉末である。特に、30nm以下の1次粒子径を有するものが光沢性の点で好ましい。

【0077】現在、このような気相法により合成された微粒子シリカは市販されており、市販の微粒子シリカには、日本エロジル社の各種のエロジルがある。

【0078】本発明で好ましく用いられるコロイダルシリカは、珪酸ナトリウムを酸等によって複分解したり、イオン交換樹脂層を通過させたりして得られるシリカゲルを加熱熟成して得られるものである。このコロイダルシリカをインクジェット記録用紙に使用することは、例えば、特開昭57-14091号公報、同60-219083号公報、同60-219084号公報、同61-20792号公報、同61-188183号公報、同63-17807号公報、同特開平4-93284号公報、同5-278324号公報、同6-92011号公報、同6-183134号公報、同6-297830号公報、同7-81214号公報、同7-101142号公報、同7-179029号公報、同7-137431号公報、及び国際特許公開WO94/26530号公報などに記載されている。

【0079】コロイダルシリカの粒子径は、通常、5~100nmであるが、粒子径7~30nmのものが好ましい。

【0080】気相法により合成された微粒子シリカやコロイダルシリカは、その表面をカチオン変成してもよく、例えば、A1、Ca、Mg及びBa等の無機塩で表面を処理してもよい。

【0081】上記空隙形成物質の中でも、本発明におい

ては微粒子シリカが特に好ましく、中でも前記〔6〕の空隙形成を行うのに最も適して微粒子は、気相法により合成されたシリカである。

【0082】上記空隙型のインク吸収層には皮膜としての特性を持たせるために親水性バインダーが用いられる。

【0083】これらのバインダーとしては膨潤型のインク吸収層に用いられる従来公知の各種のバインダーを使用することができるが、着弾したインク液滴が浸透した初期の段階で膨潤して空隙を実質的に塞いでしまわないバインダーが好ましい。この点から特に好ましい親水性バインダーは完全または部分ケン化のポリビニルアルコールである。なお、ここでいうポリビニルアルコールにはカチオン変性ポリビニルアルコール、アニオン変性ポリビニルアルコール及びノニオン変性ポリビニルアルコールも含まれる。

【0084】特に好ましいポリビニルアルコールは、ケン化度が80以上の部分ケン化ポリビニルアルコールまたは完全ケン化ポリビニルアルコールである。

【0085】ポリビニルアルコールの重合度は、皮膜脆弱性を改良する観点からすると比較的高重合度のものがよく、平均重合度が1000～5000、特に好ましくは2000～4000のものが用いられる。

【0086】カチオン変性ポリビニルアルコールとは、例えば、特開昭61-10483号公報に記載されているような、第1～3級アミノ基や第4級アンモニウム基をポリビニルアルコールの主鎖または側鎖中に有するポリビニルアルコールのことであり、カチオン性基を有するエチレン性不飽和单量体と酢酸ビニルとの共重合体をケン化することにより得られる。

【0087】カチオン性基を有するエチレン性不飽和单量体としては、例えば、トリメチル-(2-アクリラミド-2, 2-ジメチルエチル)アンモニウムクロライド、トリメチル-(3-アクリラミド-3, 3-ジメチルプロピル)アンモニウムクロライド、N-ビニルイミダゾール、N-ビニル-2-メチルイミダゾール、N-(3-ジメチルアミノプロピル)メタクリラミド、ヒドロキシルエチルトリメチルアンモニウムクロライド、トリメチル-(メタクリラミドプロピル)アンモニウムクロライド、N-(1, 1-ジメチル-3-ジメチルアミノプロピル)アクリラミド等が挙げられる。

【0088】カチオン性基を有するエチレン性不飽和单量体と酢酸ビニルとの共重合体において、カチオン変性基含有单量体の比率は、酢酸ビニルに対して0.1～10モル%、好ましくは0.2～5モル%である。

【0089】カチオン変性ポリビニルアルコールは、通常、重合度500～4000のものが用いられるが、1000～4000が好ましい。

【0090】アニオン変性ポリビニルアルコールとしては、例えば、特開平1-206088号公報に記載されているようなアニオン性基を有するポリビニルアルコール、特開昭61-237681号公報及び同63-307979号公報に記載されているようなビニルアルコールと水溶性基を有するビニル化合物との共重合体、特開平7-285265号公報に記載されているような水溶性基を有する変性ポリビニルアルコールが挙げられる。

【0091】ノニオン変性ポリビニルアルコールとしては、例えば、特開平7-9758号公報に記載されているようなポリアルキレンオキサイド基をビニルアルコールの一部に付加したポリビニルアルコール誘導体、特開平8-25795号公報に記載された疎水性基を有するビニル化合物とビニルアルコールとのブロック共重合体が挙げられる。

【0092】空隙型のインク吸収層のバインダーとしては、ポリビニルアルコールが主に用いられるが、他の親水性バインダーを含有させることもできる。他の親水性バインダーはポリビニルアルコールに対して概ね20重量%以下であることが好ましい。

【0093】インク吸収層が空隙型のインク吸収層である場合、固体微粒子の親水性バインダーに対する重量比は、空隙の形成方法で異なり、前記空隙を形成させる方法〔5〕の場合には、概ね6～100であり、空隙を形成させる方法〔6〕の場合には、2～10である。

【0094】本発明のインクジェット記録用紙において、インク吸収層中には親水性バインダーとともにカチオン媒染剤を含有する。

【0095】カチオン媒染剤としては、第1級～第3級アミノ基及び第4級アンモニウム塩基を有するポリマー媒染剤を用いることができるが、経時での変色や耐光性の劣化が少ないと、染料の媒染能が充分高いことなどから、第4級アンモニウム塩基を有するポリマー媒染剤が好ましい。

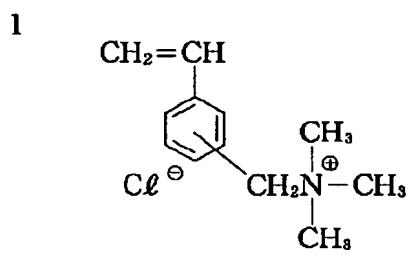
【0096】好ましいポリマー媒染剤は、第4級アンモニウム塩基を有するモノマーの単独重合体やその他のモノマーとの共重合体または縮合重合体である。

【0097】以下に、好ましく用いられる第4級アンモニウム塩基を有するモノマーの具体例を表す。

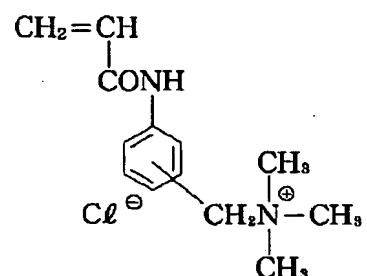
【0098】

【化1】

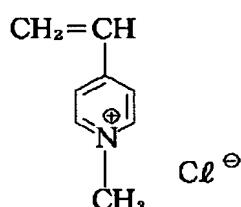
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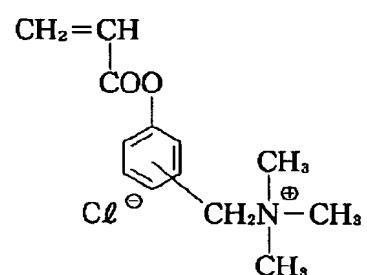
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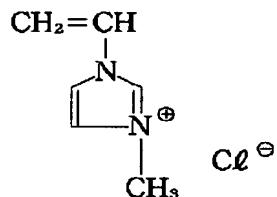
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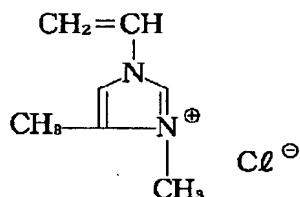
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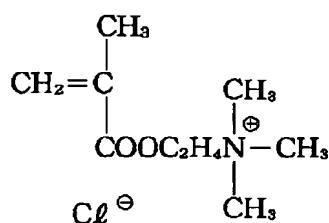
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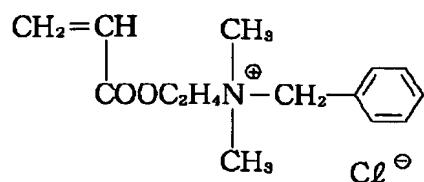


【0099】

【化2】

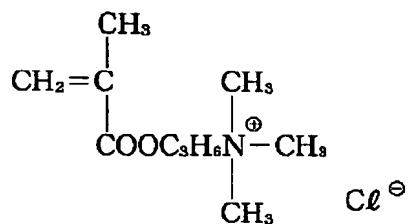
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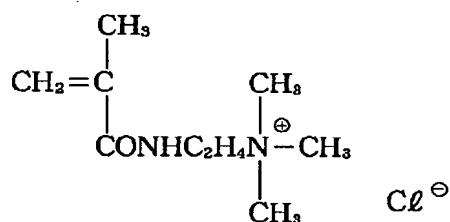


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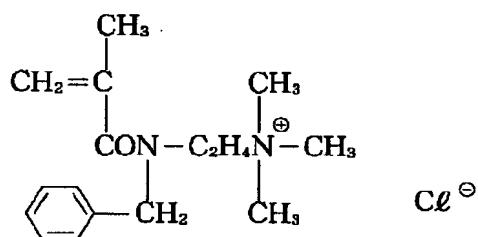
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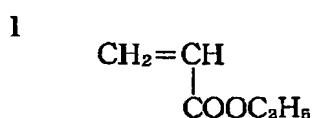
上記モノマーと共に重合し得るモノマーの具体例を次に示す。

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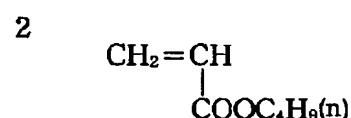
【0100】

【化3】

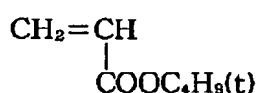
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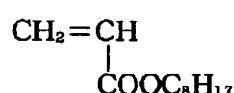
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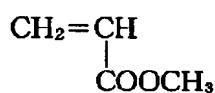
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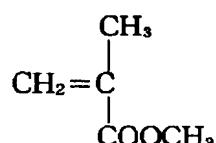
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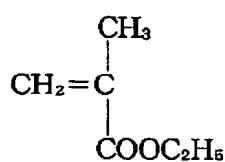
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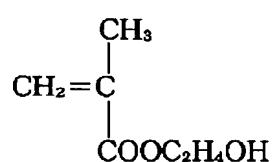
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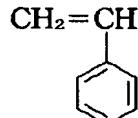
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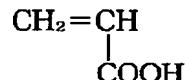
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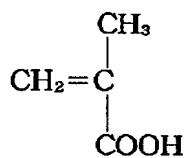
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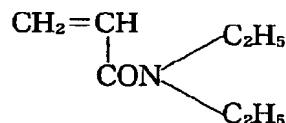
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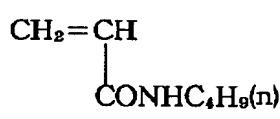
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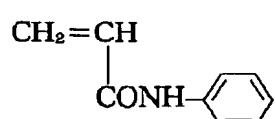
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14



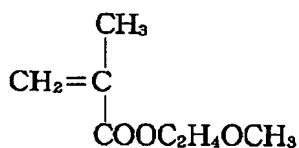
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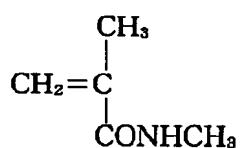


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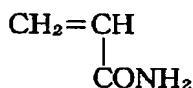
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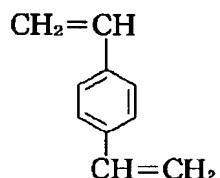
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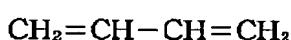
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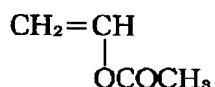
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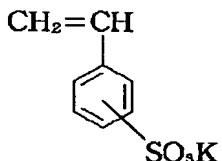
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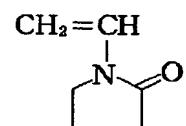
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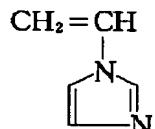
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23



24



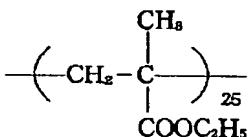
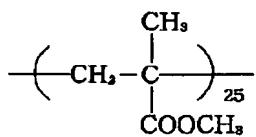
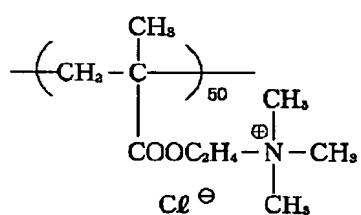
以下に好ましく用いられる第4級アンモニウム塩基を有するポリマー媒染剤の具体例を示す。（数値はモル%を表す。）

【0102】

【化5】

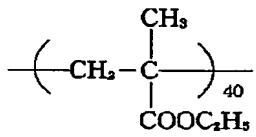
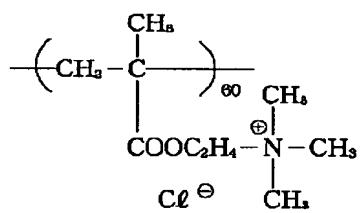
23

Mor-1

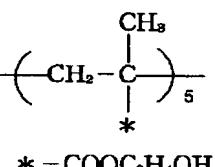
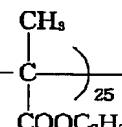
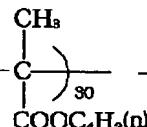
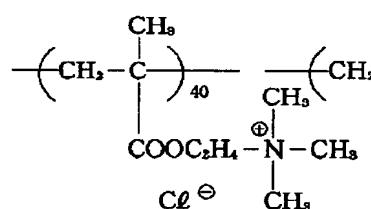
平均分子量 \approx 30,000

24

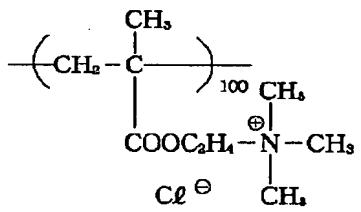
Mor-2

平均分子量 \approx 20,000

Mor-3

平均分子量 \approx 25,000

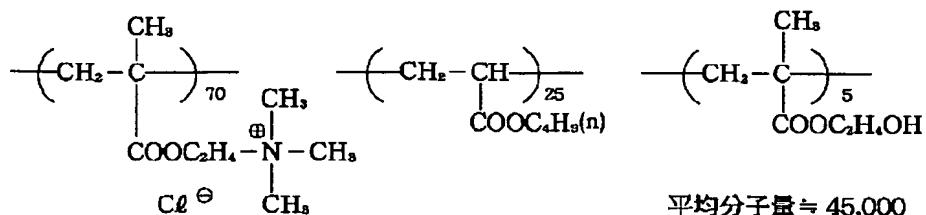
Mor-4

平均分子量 \approx 40,000

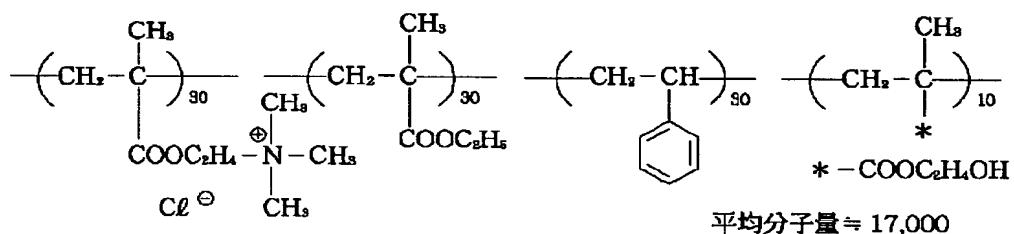
【0103】

【化6】

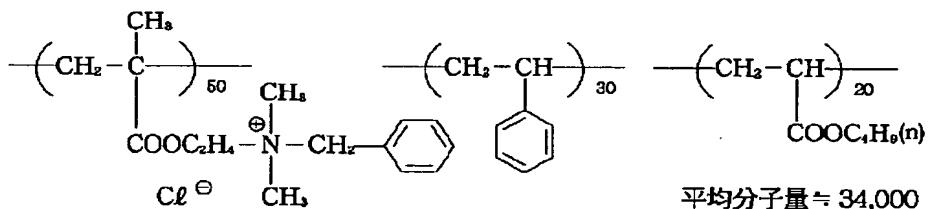
Mor-5



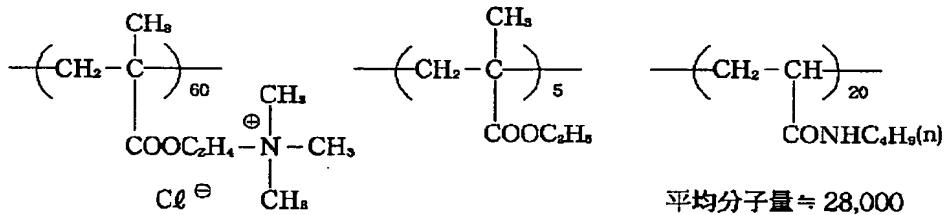
Mor-6



Mor-7

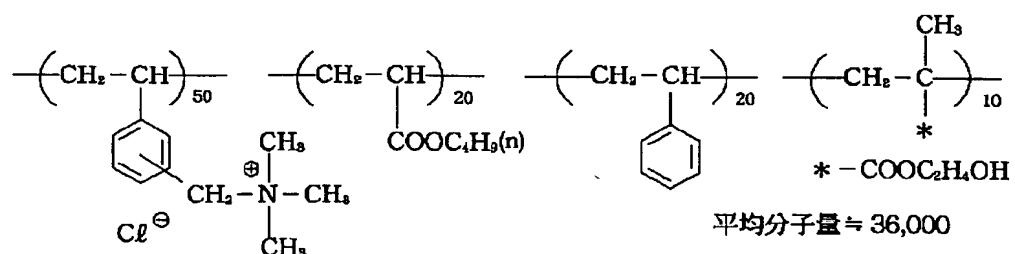


Mor-8



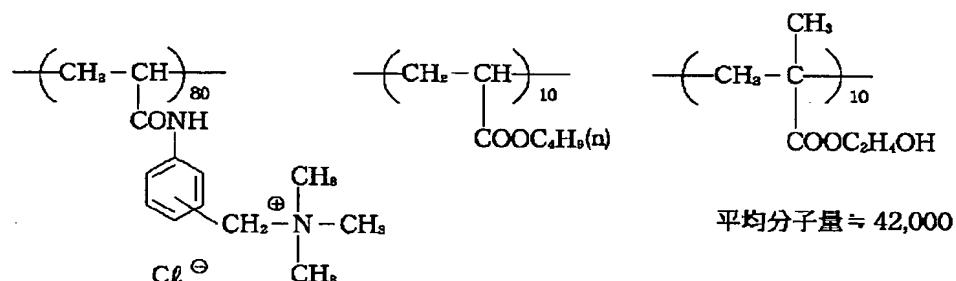
27

Mor-9

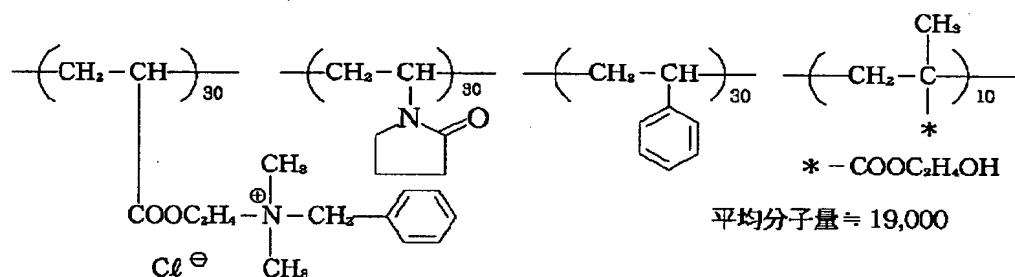


28

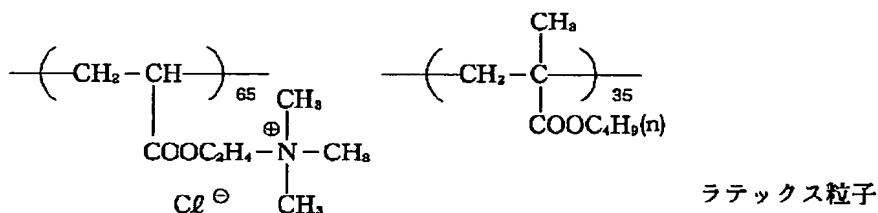
Mor-10



Mor-11



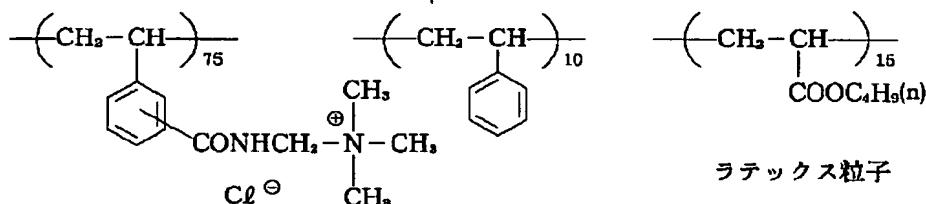
Mor-12



【0105】

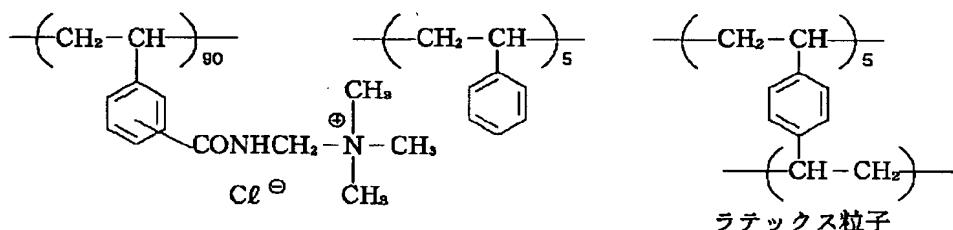
【化8】

Mor-13

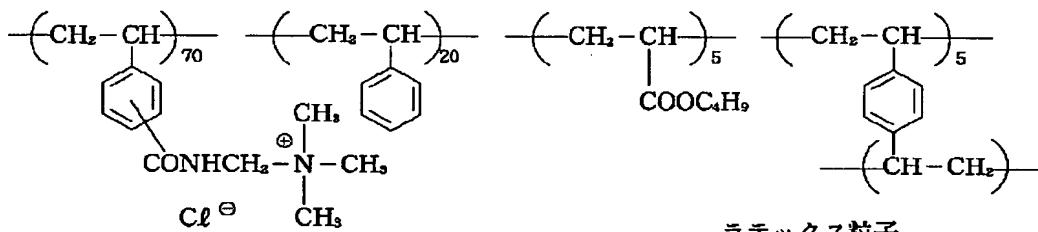


ラテックス粒子

Mor-14



Mor-15



カチオン媒染剤は、水溶性のポリマーによるポリマー媒染剤であっても、また、乳化重合で合成されたラテックス粒子によるポリマー媒染剤であってもよい。インク吸収層が膨潤型のインク吸収層である場合にはラテックス媒染剤が、また、インク吸収層が空隙型のインク吸収層である場合には水溶性のポリマー媒染剤が好ましい。

【0106】水溶性カチオン媒染剤の中でも、平均分子量が5万以下であるカチオン媒染剤が、無機微粒子との凝集が少ないため、カチオンサイトが効果的に耐水性や耐湿性の改良に寄与し、また、光沢性が劣化しにくいために好ましい。

【0107】好ましい平均分子量は3万以下である。平均分子量の下限は特に制約はないが耐水性や耐湿性の観点より大凡2000以上である。

【0108】ここで平均分子量は数平均分子量のことでありゲルバーミエーションクロマトグラフィーから求めたポリスチレン換算値をいう。

【0109】媒染剤の使用量は、インク吸収層が膨潤型か空隙型か、支持体が吸水性か非吸水性か、更には記録液の染料の濃度や記録密度等により変化するが、一般には、記録用紙1m²当たり0.2~10g、好ましくは0.5~5

gの範囲で用いられる。

30 【0110】記録用紙が空隙型であってカチオン媒染剤として水溶性ポリマーが用いられている場合には、カチオン媒染剤と無機微粒子との比率が重要であり、無機微粒子に対するカチオン媒染剤の比率が重量比で0.01~0.3であることが好ましい。

【0111】0.01未満の場合には、耐水性や耐湿性の効果が不十分になりやすく、また、0.3を超えた場合にはカールが問題になりやすい。

【0112】本発明においては、インクジェット記録用紙の記録面側の膜面pHを特定の値、即ち、3以上、5以下の範囲にすることが必要である。

40 【0113】本発明の記録用紙においては、インクジェット記録用紙の記録面側の膜面pHを特定の値に選定したため、必要最小量のカチオン媒染剤の使用により最良の耐水性と耐湿性が得られ、カチオン媒染剤の使用量は最小限に押さえることができ、カチオン媒染剤の多量使用による欠陥が生じるのを防ぐことができる。

【0114】膜面pHが3未満の場合には、耐水性や耐湿性は大幅に改善されるが、インクジェット記録する際に、記録液が記録用紙表面に接触した瞬間に染料が凝集したり、記録後経時により染料が表面に析出したりし

て、良好な最大濃度が得られなかったり、色調不良を起こしたりする。

【0115】膜面pHが5を超える時には、耐水性や耐湿性が不十分になり、特に耐湿性の低下が大きい。

【0116】膜面pHが耐湿性に影響を与える理由は定かではないが、膜面pHが5を越えると、印字後に、高湿下で保存された場合に、インク吸収層中に取り込まれた水分により染料の移動度が増大して、チオニン媒染剤が含有されていても染料が滲んでしまうのではないかと考えている。

【0117】この印字後の滲みは、印字直後から高湿下で保存した方がより顕著であり、記録液中に含まれるグリセリンやジエチレングリコール等の親水性の高沸点有機溶媒が皮膜から蒸発しきらないときにより起こりやすい。

【0118】高湿下で保存した場合、インクジェットプリンターで印字された個々のドットが経時で滲むようになるために、特にハイライト部や中間濃度域で濃度変化として現れる。

【0119】水中に浸漬した場合、膜面pHは変化してしまうと考えられるので、膜面pHが耐水性に影響を与える理由は定かではないが、膜面が特定のpHであった場合、染料が強固に媒染剤に染着し、水中に浸漬されても流れ出しにくくなるものと推定している。

【0120】本発明において、膜面pHとは、J.T.A.P.P.I紙パルプ試験方法No.49に記載の方法に従って、蒸留水を用い、30秒後に測定した表面pHをいう。

【0121】膜面pHを本件発明の範囲、即ち3以上、5以下に調節する方法としては、

①インク吸収層を形成する塗布液のpHをあらかじめ決められた値に設定しておき、塗布乾燥後に目的のpHにする方法。

②インク吸収層の塗布乾燥後に、適当なpHの液をオーバーコートし、乾燥して目的のpHを得る方法。

③インク吸収層の塗布乾燥後に、適当なpHの水溶液中に浸漬・乾燥する方法。などが挙げられる。

【0122】上記①～③の方法のうち、製造方法が簡略である点からすると①の方法が好ましい。

【0123】①の方法を実施する場合、塗布液のpHと乾燥塗膜の膜面のpHとは必ずしも一致しないため、塗布液のpHと膜面pHとの関係をあらかじめ実験等により求めておくことが目的の膜面pHにするために必要である。

【0124】膜面pHの調節は、各種の酸またはアルカリを適当に組み合わせて行われる。

【0125】酸としては、例えば、塩酸、硝酸、硫酸、磷酸等の無機酸、酢酸、クエン酸、コハク酸等の有機酸が用いられ、アルカリとしては、例えば、水酸化ナトリウム、水酸化カリウム、水酸化カルシウム、アンモニア水、炭酸カリウム、炭酸ナトリウム、磷酸三ナトリウ

ム、トリエタノールアミンなどが用いられる。

【0126】インク吸収層には、他に、種々の添加剤を添加することができる。以下、説明する。

【0127】本発明の記録用紙のインク吸収層中には、親水性バインダーを架橋し得る硬膜剤を添加することができる。

【0128】インク吸収層が膨潤型のインク吸収層である場合には、硬膜化することによりインクの吸収速度が顕著に低下するので硬膜剤の使用量は最小限度にすべきである。

【0129】インク吸収層が空隙型のインク吸収層である場合、硬膜化することにインク吸収速度が改善されるので、親水性バインダーを架橋するのが好ましい。親水性バインダーが硬膜されることによりインク吸収速度が改良されるのは、親水性バインダーのインク液に対する膨潤性が抑制され、空隙の閉塞が防止されるためである。

【0130】硬膜剤は、親水性バインダーが持っている種々の官能基と反応し得る基を有する化合物であり、例えば、エポキシ基、ホルミル基、エチレンイミノ基、活性ビニル基等を有する化合物である。

【0131】硬膜剤の添加量は上記の如くインク吸収層の違いにより大きく異なるが、膨潤型では親水性バインダー1g当たり0.1～20mg、空隙型では親水性バインダー1g当たり5～500mgである。

【0132】本発明で用いる親水性バインダーとして好ましいポリビニルアルコールにおいては、ほう酸及び/またはほう砂を硬膜剤として添加するのが好ましい。ほう酸及び/またはほう砂の使用量はポリビニルアルコール1g当たり50～500mgである。

【0133】上記以外に、例えば、特開昭57-74193号公報、同57-87988号公報及び同62-261476号公報に記載の紫外線吸収剤、特開昭57-74192号公報、同57-87989号公報、同60-72785号公報、同61-146591号公報、特開平1-95091号公報及び同3-13376号公報等に記載されている退色防止剤、アニオン、カチオンまたは非イオンの各種界面活性剤、特開昭59-42993号公報、同59-52689号公報、同62-280069号公報、同61-242871号公報及び特開平4-219266号公報等に記載されている蛍光増白剤、消泡剤、ジエチレングリコール等の潤滑剤、防腐剤、増粘剤、帯電防止剤、マット剤等の公知の各種添加剤を含有させることもできる。

【0134】本発明のインクジェット記録用紙は、インク吸収層を支持体の同一側に2層以上有していてよい。この場合、インク吸収層は、膨潤型のインク吸収層であっても、空隙型のインク吸収層であってもよい。

【0135】具体的な層構成の例として以下のものが挙げられる。

①空隙型のインク吸収層のみから成る記録用紙（空隙型のインク吸収層の重層構成を含む。）。

②膨潤型のインク吸収層のみから成る記録用紙（膨潤型のインク吸収層の重層構成を含む。）。

③膨潤型のインク吸収層が下層に設けられ、上層に空隙型のインク吸収層がある記録用紙（それぞれの層が2層以上になっている場合を含む。）。

④空隙型のインク吸収層が下層に設けられ、上層に膨潤型のインク吸収層がある記録用紙（それぞれの層が2層以上になっている場合を含む。）。

【0136】本発明のインクジェット記録用紙には、インク吸収層とは反対側に、カール防止、印字直後に重ね合わせた際のくつきやインク転写の防止をはかるために種々の種類のバック層を設けることが好ましい。

【0137】バック層は、支持体の種類や厚み、インク吸収層の構成や厚みによっても変わるが、一般には、バインダーとして親水性バインダーや疎水性バインダーが用いられる。バック層の厚みは通常は0.1～10μmの範囲である。

【0138】また、バック層には他の記録用紙とのくつき防止、筆記性の改良、さらにはインクジェット記録装置内での搬送性の改良のために表面を粗面化することができる。粗面化には、粒径が2～20μmの有機または無機の微粒子を用いることができる。

【0139】次に、本発明の記録用紙を用いてインクジェット記録するときに用いる水性記録液について説明する。

【0140】水性記録液は、通常、水溶性染料及び液媒体、その他の添加剤からなっている。水溶性染料としては、公知の、インクジェット記録で用いられている直接染料、酸性染料、塩基性染料、反応性染料あるいは食品用色素等の水溶性染料が使用できるが、直接染料または酸性染料が好ましい。

【0141】水性記録液の溶媒は、水を主体とするが、記録液が乾燥した際に染料が析出し、ノズル先端やインク供給経路で目詰まりを起こすのを防止するために、通常、沸点が約120°C以上で室温で液状の高沸点有機溶媒が添加される。高沸点有機溶媒は、水が蒸発した際に染料などの固形成分が析出し、粗大析出物が発生するのを防止する作用を有することが必要であり、そのために、水よりはるかに低い蒸気圧を有することが要求される。また、水に対する混和性が高い必要がある。

【0142】そのような目的で用いられる高沸点有機溶媒としては、例えば、エチレングリコール、プロピレングリコール、ジエチレングリコール、トリエチレングリコール、グリセリン、ジエチレングリコールモノメチルエーテル、ジエチレングリコールモノブチルエーテル、トリエチレングリコールモノブチルエーテル、グリセリンモノメチルエーテル、1, 2, 3-ブタントリオール、1, 2, 4-ブタントリオール、1, 2, 4-ペニタントリオール、1, 2, 6-ヘキサントリオール、チオジグリコール、トリエタノールアミン、ポリエチレン

グリコール（平均分子量が約300以下）等が挙げられる。また、上記した以外にも、ジメチルホルムアミド、N-メチルピロリドン等も使用できる。

【0143】これら多くの高沸点有機溶剤の中でも、ジエチレングリコール、トリエタノールアミン、グリセリン、トリエタノールアミン等の多価アルコール類、トリエチレングリコールモノブチルエーテル等の多価アルコールの低級アルキルエーテル等は好ましいものである。

【0144】水性インクが含有するその他の添加剤としては、例えば、pH調節剤、金属封鎖剤、防カビ剤、粘度調整剤、表面張力調整剤、潤滑剤、界面活性剤、及び防錆剤、等が挙げられる。

【0145】水性インクは、記録用紙に対する濡れ性を良好にしたり、インクジェットノズルからの吐出を安定化させる目的で、25°Cにおいて、25～50dyne/cm、好ましくは28～40dyne/cmの範囲内の表面張力を有するのが好ましい。

【0146】また、水性インクの粘度は、通常25°Cにおいて2～10cpが好ましく、更に好ましくは2.5～8cpである。

【0147】本発明のインクジェット記録方法においては、記録液のpHを3以上、8以下にすることが本発明の効果を最大限引き出すのに好ましい。

【0148】記録液のpHを8以下にすることで、本発明のインクジェット記録用紙と組み合わせた場合、特に、相対湿度が80%を超える環境で記録され、そのままの状態で保存された場合、耐湿性に対する改良効果が大きくなる。

【0149】記録液のpHが3未満になると、水溶性染料の安定性が低下して目詰まりを起こしやすくなったり、インクジェットプリンター内のインク給液経路にある各種の材質を腐食し易くなったりする。

【0150】更に好ましい記録液のpHは3.5～7である。

【0151】インクノズルから吐出されるインク液滴の容量が1～30pLである場合、記録紙上で約20～60μmの直径のドット径が得られるので好ましい。このようなドット径で印字されたカラープリントは高画質の画像を与える。更に好ましいインク液滴の容量は2～20pLである。

【0152】また、少なくともマゼンタ及びシアンにおいて、濃度が2倍以上異なる2種類の水性記録液を用いた記録方式でインクジェット記録する場合、ハイライト部では低濃度のインクが使用されるためにドットの識別がしにくくなるが、本発明はかかる記録方式を用いた場合にも、これらの欠点が生じることはない。

【0153】インクジェット記録方法において、記録方法としては、従来公知の各種の方式を用いることができる。記録方法の詳細は、例えば、インクジェット記録技術の動向（中村孝一編、平成7年3月31日、日本科学情

報株式会社発行)に記載されている。

【0154】

【実施例】以下に、本発明を実施例により具体的に説明するが、本発明はこれらの実施例によって限定されるものではない。

【0155】実施例1

160g/m²の写真用原紙の両面をポリエチレンで被覆した紙支持体(記録面側には、厚さ35μmのアナターゼ型二酸化チタンを13重量%含有するポリエチレン層が形成されており、裏面側には厚みは25μmでポリエチレン層が形成され、その上にTg=65°Cのアクリル系ラテックス樹脂を固体分として0.6g/m²及び平均粒径が約13μmのシリカをマット剤として0.3g/m²含有するバック層が形成されている。)を用意した。

〈塗布液1-1の作製〉純水900ml中に、1次粒子の平均粒径が約7nmの気相法により合成された微粒子シリカ粉末180gを高速ホモジナイザーで攪拌しながら添加しシリカ水分散液を作製した。次に、このシリカ水分散液中に、例示媒染剤M or-1(カチオン媒染剤)の25%水溶液を100ml添加し、30分間高速ホモジナイザーで分散して青白い透明な分散液を得た。次に、平均重合度が300でケン化度が88%の10%ポリビニルアルコール水溶液を1ml添加し、更に、平均重合度が3500でケン化度が88%の5%ポリビニルアルコール水溶液(酢酸エチルを4重量%含有)530mlを徐々に添加した。次いで、硬膜剤として4%ほう酸水溶液40mlを添加し、また、20mlのエタノールを添加し、更に、10%ゼラチン水溶液を50ml加えて空隙型のインク吸収層を形成する塗布液1-1を作製した。

〈記録用紙1-1の作製〉40°Cに加温した塗布液1-1を、上記の両面をポリエチレンで被覆した紙支持体の記録面側に湿潤膜厚が260μmになるように塗布し、塗布皮膜温度が15°C以下になるように冷却した(20秒間)。次いで、25°Cの風を60秒間、30°Cの風を60秒間、40°Cの風を60秒間、50°Cの風を120秒間、更に35°Cの風を60秒間順次吹き付けて乾燥し、更に、25°C、相対湿度50%の雰囲気を120秒間通過させて調湿して記録用紙1-1を作製した。

(マゼンタインクの記録液の組成)

純水	75ml
ジエチレングリコール	10.3g
グリセリン	7.3g
C ₉ H ₁₉ O (C ₂ H ₅ OCH ₂ O) ₁₀ H	0.05g
Direct Red 227	1.7g

水酸化ナトリウム/硫酸でpH=5.0±0.1に調整した後、純水にて100mlに仕上げる。

〈6〉耐湿性

記録用紙に、23°C、相対湿度80%の環境下で、オンデマンド型インクジェットプリンターを用い、上記組成のマゼンタインクの記録液で、反射濃度が約0.5になるよう

【0156】得られた記録用紙1-1の膜面pHを表1に示す。

〈記録用紙1-2~1-5の作製〉塗布液1-1のpHを硝酸または水酸化ナトリウムを用いて変化させ、記録用紙1-1と同様にして、記録用紙1-2~1-5を作製した。

【0157】得られた記録用紙1-2~1-5の膜面pHを表1に示す。

【0158】得られた記録用紙1-1~1-5について、空隙容量、インク吸収性、光沢度、カール、耐水性、耐湿性、耐光性、最高濃度を下記により評価した。

〈1〉空隙容量

熊谷理機工業株式会社製、Bristow試験機II型(加圧式)を使用し、接触時間2秒間における転移量(ml/m²)を空隙容量として求めた。

〈2〉インク吸収性

熊谷理機工業株式会社製、Bristow試験機II型(加圧式)を使用し、接触時間が0.5秒における転移量(ml/m²)からインク吸収性を求めた。

〈3〉光沢度

日本電色工業株式会社製変角光度計(VGS-101DP)で75度鏡面光沢を測定した。

〈4〉カール

23°C、相対湿度が20%の環境と、30°C、相対湿度が80%の環境に、A5サイズの試料を30分間放置し、4隅の高さを測定し、その平均値を求め、カールを評価した。記録面を上側にして記録用紙を台上に載置したとき、記録用紙の端部が台上より高ければ+、記録面を下側にして記録用紙を台上に載置したとき、記録用紙の端部が台上より高ければ-としてカールの高さを表示した。この高さが±10mm以下で有れば概ね実用上問題がない。

【0159】〈5〉耐水性

記録用紙に、オンデマンド型インクジェットプリンターを用い、下記組成のマゼンタインクの記録液で反射濃度が約1.0になるように印字した。印字後、室温で純水中に12時間浸漬してから反射濃度を再度測定した。

【0160】純水に浸漬する前の反射濃度に対して浸漬後の反射濃度の残存率を求め、耐水性とした。

75ml

10.3g

7.3g

0.05g

1.7g

に印字した。印字後、そのままの状態で48時間放置した。印字直後の反射濃度に対する放置後の反射濃度の変化率(0%が濃度変化なし)を調べ、耐湿性とした。

〈7〉耐光性

記録用紙に、オンデマンド型インクジェットプリンターを用い、上記組成のマゼンタインクの記録液で反射濃度

が約1.0になるように印字した。キセノンフェードメーターを用い、印字した記録用紙に100時間光照射し、光照射後の反射濃度を測定し、光照射前の反射濃度に対する光照射後の反射濃度の比率を色素残存率として求め、耐光性とした。

〈8〉最高濃度

記録用紙に、オンデマンド型インクジェットプリンター

記録用紙	膜面pH	空隙容量	インク吸収性	光沢度	カール (mm)		耐水性 (%)	耐湿性 (%)	耐光性 (%)	最大濃度
					23°C/20%	30°C/80%				
1-1 比較例	5.5	38.0	24.0	62.0	+3.0	-3.0	83.4	+25	72	2.09
1-2 本発明	4.5	37.5	24.5	62.7	+3.0	-2.5	89.6	+7	70	2.04
1-3 本発明	4.0	37.5	23.5	63.3	+3.5	-3.0	90.4	+4	70	2.05
1-4 本発明	3.5	37.0	23.0	61.8	+2.5	-2.0	92.2	+2	69	2.00
1-5 比較例	2.5	37.5	23.5	63.6	+2.5	-3.0	95.3	+2	63	1.73

【0163】表1の結果から、膜面pHを3~5の範囲に調整した記録用紙1-2~1-4は空隙容量・インク吸収性・光沢度・カール・耐光性に殆ど悪影響を与えることなく耐湿性と耐水性をともに改良していることがわかる。

【0164】これに対して、膜面pHが5.5である記録用紙1-1は耐水性が若干低く、特に耐湿性がカチオン媒染剤を含有しているのにも係わらず劣っている。また、膜面pHを2.5にした記録用紙1-5は耐水性や耐湿性は優れているものの染料の結晶化に伴うと見られる最大濃度の顕著な低下が認められる。

記録用紙	膜面pH	空隙容量	インク吸収性	光沢度	カール (mm)		耐水性 (%)	耐湿性 (%)	耐光性 (%)	最大濃度
					23°C/20%	30°C/80%				
2-1 比較例	5.7	39.0	26.0	63.6	+6.5	-5.0	86.2	+22	70	2.02
2-2 本発明	4.8	38.5	26.5	84.1	+7.0	-5.5	91.2	+8	69	2.01
2-3 本発明	4.2	38.0	25.5	64.3	+7.5	-6.5	94.4	+2	68	2.01
2-4 本発明	3.7	38.5	26.0	63.7	+6.5	-5.0	96.2	+2	68	1.97
2-5 比較例	2.8	38.5	24.5	64.2	+7.5	-6.5	97.3	+2	64	1.65

【0167】表2の結果から、カチオン媒染剤をカチオンモノマー単独重合体である例示媒染剤M or -4に変更した場合にも、実施例-1と同様の効果が得られることがわかる。

【0168】例示媒染剤M or -4を使用した場合、例示媒染剤M or -1に比較してカール特性が若干低下するが、耐水性と耐湿性が向上している。

【0169】実施例-3

〈塗布液3-1の作製〉1次粒子の平均粒径が約20nmの20%コロイダルシリカ水溶液900mlに純水100mlを加え、

を用い、下記組成のマゼンタインクの記録液で、マゼンタの最高濃度が得られる条件で印字し、その反射濃度を測定し、最高濃度とした。

【0161】以上の結果を表1に示した。

【0162】

【表1】

【0165】実施例-2

20 例示媒染剤M or -1を例示媒染剤をM or -4に変更した以外は実施例-1と同様にして、表2に示す膜面pHを有する記録用紙2-1~2-5を作製した。得られた記録用紙2-1~2-5について、実施例-1と同様にして、空隙容量、インク吸収性、光沢度、カール、耐水性、耐湿性、耐光性、最高濃度を評価した。得られた結果を表2に示す。

【0166】

【表2】

高速ホモナイザーで攪拌しながら例示媒染剤M or -1の25%水溶液を150ml添加し、更に30分間高速ホモナイザーで分散して青白い澄明な分散液を得た。次に、平均重合度が300でケン化度が88%の10%ポリビニルアルコール水溶液を2mlを添加し、更に平均重合度が3500でケン化度が88%の5%ポリビニルアルコール水溶液（酢酸エチルを4重量%含有）650mlを徐々に添加した。次いで、硬膜剤として4%ほう酸水溶液40mlを添加し、また、20mlのエタノールを添加し、更に、10%ゼラチン水溶液を50ml加えて空隙型のインク吸収層を形成す

る塗布液3-1を作製した。

〈記録用紙3-1~3-5の作製〉上記塗布液3-1を用い、実施例-1で使用した支持体上に、実施例-1と同様にして塗布・乾燥して、表3に示す膜面pHを有する記録用紙3-1を作製した。更に、実施例-1と同様にして、膜面pHを表3に示すようなるように変化させた記録用紙3-2~3-5を作製した。

記録用紙	膜面pH	空隙容量	インク吸収性	光沢度	カール(mm)		耐水性(%)	耐湿性(%)	耐光性(%)	最大濃度
					23°C/20%	30°C/80%				
3-1 比較例	5.4	31.0	19.5	57.3	+3.5	-3.5	80.1	+32	62	2.17
3-2 本発明	4.6	31.5	20.0	56.3	+3.0	-3.5	86.2	+9	61	2.15
3-3 本発明	4.1	32.0	20.0	57.8	+3.5	-3.5	88.3	+6	61	2.15
3-4 本発明	3.5	31.5	19.5	57.4	+2.5	-4.0	89.5	+4	63	2.13
3-5 比較例	2.5	31.0	19.5	57.2	+3.5	-3.5	90.7	+4	62	1.82

【0172】表3に示す結果から、気相法により合成されたシリカに代えてコロイダルシリカを用いた場合、空隙容量が低下するが、実施例-1と同様に膜面pHを3~5にした記録用紙3-2~3-4は最大濃度を低下させずに耐水性と耐湿性を改良していることがわかる。

【0173】実施例-4

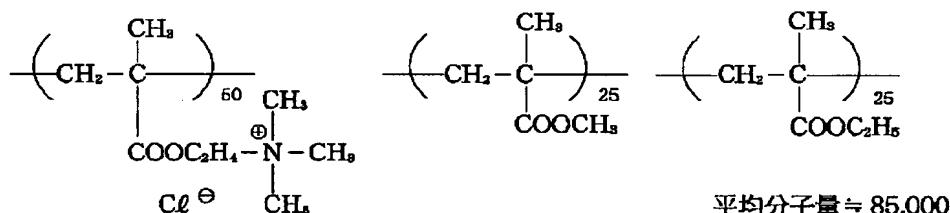
1次粒子の平均粒径が約7nmの気相法により合成された微粒子シリカ粉末に代えて、1次粒子の平均粒径が12nm、20nm及び50nmの気相法により合成された微粒子シリカ粉末を用いた。

力粉末を用いた以外は、実施例-1の記録用紙1-3と同様にして記録用紙4-1~4-3を作製した。

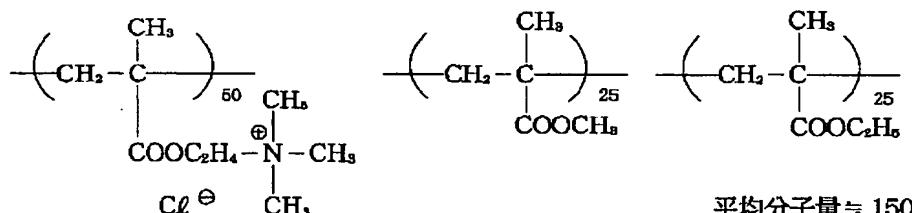
【0174】また、例示媒染剤Mor-1を下記の媒染剤-A及び-Bに変更した以外は、実施例-1の記録用紙1-3と同様にして記録用紙4-4及び4-5を作製した。

【0175】

【化9】



媒染剤-B



得られた記録用紙4-1~4-5の膜面pHを表4に示す。

【0176】また、得られた記録用紙4-1~4-5について、実施例-1と同様にして、空隙容量、インク吸

収性、光沢度、カール、耐水性、耐湿性、耐光性、最高濃度を評価した。得られた結果を表4に示す。

【0177】

【表4】

記録用紙		膜面pH	空隙容量	インク吸収性	光沢度	カール (mm)		耐水性 (%)	耐湿性 (%)	耐光性 (%)	最大濃度
						23°C/20%	30°C/80%				
4-1	本発明	4.1	36.5	22.0	62.7	+3.5	-3.5	91.3	+6	71	2.03
4-2	本発明	4.0	35.0	22.5	59.2	+2.0	-3.0	93.7	+4	70	2.01
4-3	本発明	4.1	32.0	21.5	48.2	+2.0	-3.5	95.2	+4	68	1.96
4-4	本発明	4.0	37.5	24.5	42.3	+3.5	-4.0	92.5	+4	70	2.01
4-5	本発明	4.1	38.5	23.0	31.4	+3.0	-3.0	93.1	+4	68	1.99

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【0178】表4に示すように、記録用紙4-1～4-5のいずれもカールや耐光性、最大濃度を低下させずに高い耐水性と耐湿性を有している。

【0179】また、気相法により合成された微粒子シリカ粉末の1次粒子の平均粒径が増大すると徐々に空隙容量と光沢性が低下し、好ましいシリカの1次粒子の平均粒径は約30nm以下であることがわかる。

【0180】また、媒染剤として分子量の高いものを使用した場合には徐々に光沢が低下していくことがわかる。記録用紙4-4及び4-5を作製するのに使用した塗布液には微小な凝集物が発生しておりこれが光沢低下の原因である。

【0181】実施例-5

気相法により合成された微粒子シリカ(シリカ)とポリ

ビニルアルコール(PVA)の比率を表5に示すように変化させた以外は、実施例-1の記録用紙1-3と同様にして、記録用紙5-1～5-4を作製した。

【0182】得られた記録用紙5-1～5-4の膜面pHを表4に示す。

【0183】また、得られた記録用紙5-1～5-4について、実施例-1と同様にして、空隙容量、インク吸収性、光沢度、カール、耐水性、耐湿性、耐光性、最高濃度を評価した。得られた結果を表5に示す。

【0184】また、表5には、参考のために記録用紙1-3の膜面pH、空隙容量、インク吸収性、光沢度、カール、耐水性、耐湿性、耐光性、最高濃度を示した。

【0185】

【表5】

記録用紙		(VMA/PVA)比	膜面pH	空隙容量	インク吸収性	光沢度	カール (mm)		耐水性 (%)	耐湿性 (%)	耐光性 (%)	最大濃度
							23°C/20%	30°C/80%				
1-3	本発明	7.2	4.0	37.5	23.5	63.3	+3.5	-3.0	90.4	+4	70	2.05
5-1	本発明	10.5	3.9	40.5	28.5	42.2	+5.0	-5.5	93.2	+7	84	1.97
5-2	本発明	5.0	4.0	34.5	18.5	66.5	+3.0	-2.0	89.3	+4	72	2.05
5-3	本発明	3.0	4.1	31.0	14.0	69.2	+2.0	-1.5	87.4	+4	74	2.09
5-4	本発明	1.5	4.0	23.0	10.5	73.2	+2.0	-1.5	86.3	+4	78	2.11

【0186】表5に示すように、記録用紙5-1～5-4のいずれもカールや耐光性、最大濃度を低下させずに高い耐水性と耐湿性を有している。

【0187】気相法により合成された微粒子シリカ粉末のポリビニルアルコールに対する比率を10以上にした記録用紙5-1は空隙容量が大きくなり、インク吸収性が改善されているが、全面に微小なクラックが発生して光沢が低下している。また、気相法により合成された微

子シリカ粉末のポリビニルアルコールに対する比率を2以下にした記録用紙5-4では空隙容量が低下している。

【0188】実施例-6

〈塗布液6-1の作製〉塗布液1L当たり以下の成分を含有する塗布液6-1を作製した。

【0189】

酸処理ゼラチン	38 g
ポリビニルピロリドン (K-90)	12 g
ポリエチレンオキサイド (平均分子量=約15万)	10 g
媒染剤 (例示媒染剤Mort-15)	32 g
カチオン性蛍光増白剤	0.1 g
硬膜剤 (H-1)	0.2 g

〈記録用紙6-1の作製〉得られた塗布液6-1を、150g/m²の写真用原紙の両面をポリエチレンで被覆した紙支持体（記録面側には厚さ35μmのアナターゼ型二酸化チタンを13重量%含有するポリエチレン層が形成されおり、裏面側には厚さ25μmのポリエチレン層が形成され、その上にゼラチン2.2gと平均粒径が約2μmのシリカをマット剤として0.1g/m²含有するバック層が形成されている。）の記録面側に湿潤膜厚が120μmに成るよう¹⁰に塗布し、冷却セットした後、乾燥して記録用紙6-1を得た。

【0190】得られた記録用紙6-1の膜面pHを表6に示す。

記録用紙		膜面pH	光沢度	カール (mm)		耐水性 (%)	耐湿性 (%)	耐光性 (%)	最大濃度
				23°C/20%	30°C/80%				
6-1	比較例	5.4	62.0	+8.0	-6.0	84.7	+19	79	2.12
6-2	本発明	4.6	62.7	+7.5	-8.5	87.1	+8	77	2.13
6-3	本発明	4.1	63.3	+9.0	-7.0	89.2	+4	78	2.15
6-4	本発明	3.6	61.8	+8.5	-6.5	90.5	+4	77	2.12
6-5	比較例	2.5	63.6	+8.5	-7.0	92.1	+2	76	1.53

表6の結果から、インク吸収層が膨潤型の場合であっても、空隙型のインク吸収層と同様の効果が得られることがわかる。

【0194】比較例-1

例示媒染剤M or-1の量を表7に示すように変化させ、また、膜面pHが表7に示すようになるようにした以外は、実施例-1の記録用紙1-1と同様にして、記録用紙7-1～7-3を作製した。なお、気相法により合成された微粒子シリカ粉末及びポリビニルアルコールの塗布量が一定になるようにした。従って、例示媒染剤M or-1の量を増加させるに伴い、膜厚が厚くなっている。

〈記録用紙6-2～6-5の作製〉塗布液6-1のpHを硝酸または水酸化ナトリウムを用いて変化させ、記録用紙6-1と同様にして、記録用紙6-2～6-5を作製した。

【0191】得られた記録用紙6-2～6-5の膜面pHを表6に示す。

【0192】また、得られた記録用紙6-1～6-5について、実施例-1と同様にして、光沢度、カール、耐水性、耐湿性、耐光性、最高濃度を評価した。得られた結果を表6に示す。

【0193】

【表6】

【0195】得られた記録用紙7-1～7-3の膜面pHを表7に示す。

【0196】得られた記録用紙7-1～7-3について、実施例-1と同様にして、空隙容量、インク吸収性、光沢度、カール、耐水性、耐湿性、耐光性、最高濃度を評価した。得られた結果を表7に示す。

【0197】また、表7には、参考のために記録用紙1-1の媒染剤量、膜面pH、空隙容量、インク吸収性、光沢度、カール、耐水性、耐湿性、耐光性、最高濃度を示した。

【0198】

【表7】

記録用紙		媒染剤量 (ml)	膜面pH	空隙容量	インク吸収性	光沢度	カール (mm)		耐水性 (%)	耐湿性 (%)	耐光性 (%)	最大濃度
							23°C/20%	30°C/80%				
1-1	比較例	100	5.5	38.0	24.0	62.0	+3.0	-3.0	83.4	+25	72	2.09
7-1	比較例	150	5.8	38.5	22.5	63.2	+9.5	-6.5	87.0	+21	80	2.08
7-2	比較例	200	5.6	35.0	20.5	63.7	+14.5	-10.0	91.3	+15	51	2.06
7-3	比較例	300	5.7	32.5	18.0	64.1	+21.0	-15.0	92.2	+11	37	2.08

【0199】表7に示すように、膜面pHが5以上であった場合でも、カチオン媒染剤の量を増量すると耐水性、耐湿性は大きく改善されるが、膜面pH 5以下にしたとき程には耐湿性を改良することはできない。また、

カチオン媒染剤の量を増量するとカールが大きくなり、耐光性が急激に悪化する。

【0200】

【発明の効果】本発明のインクジェット記録用紙は、カ

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チオン媒染剤の使用量が少なくても充分高い耐水性や耐湿性が達成でき、カチオン媒染剤の使用によってもたら

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されるカールの増大、耐光性の低化、汚染等の悪影響を最小限に押さえることができる。

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